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ADSORPTION OF BIOCHEMICALLY RESISTANT MATERIALS FROM SOLUTION. 2.

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ADSORPTION OF BIOCHEMICALLY RESISTANT MATERIALS FROM SOLUTION. 2.

by

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for

The Advanced Waste Treatment Research Activities
Cincinnati Water Research Laboratory
Robert A. Taft Sanitary Engineering Center

This publication, a combination of reports submitted by the authors in June 1963 and August 1964, is a report on the continuation of studies under Contract No. SAph 76295, between the Public Health Service and the Division of Engineering and Applied Physics, Harvard University.

Federal Water Pollution Control Administration
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Cincinnati, Ohio

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Public Health Service Publication No. 999-WP-33

ADVANCED WASTE TREATMENT RESEARCH PROGRAM

The Advanced Waste Treatment Research Activities of the Federal Water Pollution Control Administration has two ultimate goals: One is to help abate our Nation's growing water pollution problems, and the other, more startling in concept, is to renovate waste water for direct and deliberate re-use.

Conventional water and waste treatment practices have little or no effect on many simple inorganic salts and permit an ever-increasing number and amount of highly complex, synthetic organic wastes to contaminate drinking water supplies. If we are to protect these water supplies for the future, it is mandatory that new technologies for water and waste treatment be developed.

Advanced waste treatment may be looked upon as a two-step process: (1) Separating concentrated contaminants from the purified water "product," and (2) disposing of the concentrated contaminants in a way that will render them forever innocuous. This "permanent disposal" of separated wastes is essential so that useable surface or ground waters will not be contaminated and so that the same contaminants need not be removed again and again from water supplies.

In one step, then, advanced waste treatment, i.e., water renovation, could alleviate both water pollution and water supply problems — problems of increasing concern both in this country and in the rest of the world. The importance of advanced waste treatment was recognized by Congress in its 1961 amendments to the Federal Water Pollution Control Act (Public Law 87-88). This act directs the Secretary of Health, Education, and Welfare ". . . to develop and demonstrate practicable means of treating municipal sewage and other water-borne waste to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for re-use."

It is too early to predict accurately the cost of advanced waste treatment technology, but the need is inevitable. Because of population increase and industrial expansion, we are approaching the time when our rivers and streams will no longer be able to assimilate our wastes and when there will be no more developable supplies of fresh water. Whatever the cost of this technology, one thing is certain — it must be the very lowest science and engineering can achieve. Anything more

will impose an inexcusable, perhaps intolerable burden on our country's economic growth and on its ability to compete in tomorrow's world.

The authors of this report collaborated on two previous reports in this series (AWTR-2 and AWTR-9). This report, together with AWTR-9 (999-WP-11), presents the results of 3 years of work on the contract by the authors at Harvard University.

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ABSTRACT

Earlier studies (reported in PHS Publication No. 999-WP-11 - AWTR-9) showed that activated carbon for waste water renovation could best be used in continuous-flow columns. Such techniques should result in an adsorptive capacity of greater than 10 percent. Results on studies of adsorption of organics from single- and multi-component systems in fluidized carbon are reported herein. The adsorbability of organic pesticides on activated carbon was investigated in some detail. Studies were undertaken to characterize those types of organic pollutants that are not adsorbed on activated carbon.

ADSORPTION OF BIOCHEMICALLY RESISTANT MATERIALS FROM SOLUTION. 2.

Introduction

This is the second and final report, covering the last 2 years of work, on a contract with Harvard University initiated in May of 1961. The first year's work was covered in an earlier report (No. 999-WP-11) in this series. In our second contract year with the Advanced Waste Treatment Research Activities, studies were directed toward the definition and evaluation of the characteristics of adsorption from aqueous solution in columns of fluidized media. During the third year, the types of studies begun in the previous years were extended.

The first three sections of this report deal with the use of activated carbon and activated aluminum oxide to remove organic contaminants that might be found in a municipal secondary effluent. To minimize analytical complications and allow closer interpretation of results, a synthetic solution of one or more organic compounds in water was used as the feed material.

To take advantage of the previously determined fact that the adsorption rate is inversely proportional to the size of the adsorbent granule, the investigators utilized a fluidized column technique. This allowed the use of small granules without the attendant problem of plugging that would be encountered in downflow operation.

To supplement and strengthen the findings reported earlier on the effect of adsorbent particle size on adsorption rate and capacity, the authors conducted additional experiments on batch-type systems. These studies also involved single- and multi-component systems.

Because of the increasing occurrence of organic pesticides in water and waste water, the batch adsorption studies were extended to include pesticides. Analytical procedures were developed for determining concentrations of various compounds typically found in commercially available herbicides, acaricides, and insecticides.

In the early work on adsorption of organics from municipal waste water, a significant amount of the organic material, as measured by chemical oxygen demand, remained unadsorbable in activated carbon regardless of the amount of contact time. Identification of these unadsorbed materials was of interest, and so samples of carbon treated effluent were concentrated up to 60-fold and sent to Harvard for exam-

ination. A preliminary study of these concentrates indicated that the organic content was composed primarily of partially oxidized substrates and metabolites of microorganisms.

Because of the wide scope of the research and the vast number of organic materials that might be involved, none of the research projects that have been pursued, except possibly the determination of organic carbon (not reported herein), have been concluded with definitive thoroughness. A great deal has been learned about the characteristics of adsorption from dilute aqueous solution, but the information is not complete enough for conclusive generalizations. Many gaps remain in the data, and the implications of some studies have not been followed up sufficiently. Numerous instances are pointed out in this report.

Nonetheless, the fundamental ground work has been laid for more detailed and extended studies of adsorption by activated carbon on a larger scale. Advantageous possibilities for the use of activated carbon in adsorption have been shown; more practical studies are now needed to define efficient and economical conditions and procedures of operation.

This does not mean that fundamental studies in this area should be abandoned. New basic information and theory are always needed for stimulation and understanding. These studies should be undertaken now in smaller areas of interest, however, and with greater thoroughness and refinement.

ADSORPTION IN COLUMNS OF FLUIDIZED MEDIA

Previous studies of the kinetics of adsorption from solution on granular adsorbents in agitated nonflow systems have shown that particle size is an important determinant of the rate of uptake of organic substances by an adsorbent.[1] Within the range of experimentation in these previous investigations, rate of uptake was found to vary as the inverse square of the diameter of the adsorbent particle. Hence, for application of adsorption to treatment of waters and waste waters, keeping particle sizes as small as conditions of efficient operation allow appears desirable so that high rates of adsorption may be attained. Columnar operation in which the solution to be treated flows upward through an expanded bed of fine particulate adsorbent is one method of taking advantage of small particle size while avoiding the problems of excessive headloss common to standard packed-bed operation with fine media. Furthermore, other problems common to packed beds, such as air binding and fouling with particulate matter, are not usually encountered with fluid-bed operation. Design of a continuously operating, countercurrent, fluidized bed should be relatively simple. Fresh solid adsorbent may be added at the top of the column and spent adsorbent withdrawn from the bottom on a continuous basis, possibly by a lift-screw arrangement, while the solution from which adsorption is taking place flows upward from partially utilized adsorbent to freshly added material. Segregation of the adsorbent so that nearly its full capacity can be realized with this form of operation is aided by the fact that porous adsorbent particles -- of activated carbon, at least -- become denser with increasing adsorption, and tend, therefore, to concentrate in the lower strata.

Fluidization as a method of columnar operation for achieving improved fluid - solid contact has found most extensive investigation and application in the areas of heat transfer,[2-6] mass transfer in gas - solid systems,[2,5,7,8] and catalytic reactors.[2,9,10] Because of its rather extensive use in the aforementioned applications, fluidization has also been treated in great detail from the point of view of mechanics by a number of investigators.[11-15] Reports of fluidized-column operations in which the primary function of the solid has been adsorption have, however, been few; even these few have dealt principally with gas-phase adsorption and have thus had no particular significance for adsorption of organic materials from aqueous solution. Perhaps the closest example has been the use of a fluidized column of charcoal for removal of hydrocarbons from a stream of gas.[16] Much of the work that has been carried out with liquid - solid systems has dealt with the dissolution of a soluble solid rather than with the uptake of a solute by the solid.[17,18]

The kinetics of adsorption was investigated in terms of uptake profiles relative to the velocity dimensions, time and length, for selected values of these variables and for variously sized particles of adsorbent.

Two different types of adsorbent, activated carbon and activated aluminum oxide, were investigated. In the initial column studies, only single-solute solutions were used in order to facilitate interpretation of the relative significance of more fundamental variables. Later, column studies were undertaken with multicomponent solutions to observe how solutions more nearly resembling waste waters behave in continuous-flow operation.

Experimental

APPARATUS

A schematic representation of the experimental equipment is shown in Figure 1. The column, a 1-inch-diameter Lucite tube, 3 feet in length, is fitted at the bottom with a velocity-head dissipation chamber filled with 2-millimeter glass beads. In runs in which a greater quantity of carbon was used, longer columns were needed to allow ample head space for expansion. A 140-mesh stainless-steel screen separates the adsorbent in the column from the glass beads in the dissipation chamber. Sampling ports are positioned at 3-inch intervals along the length of the column. Flow to the column is regulated by means of two valves, one of which is a needle valve, in the 0.5-inch-diameter feedline from the constant-head tank. A float valve in the constant-head tank controls the flow from two 200-liter plastic storage reservoirs. Flow from the top of the column passes through an air gap, to prevent siphoning and pressure fluctuations in the column, through a 1-liter settling tank, for removal of any fine material that may have been carried over into the effluent, and into one of several volume-calibrated 200-liter collection reservoirs.

ADSORBENTS AND ADSORBATES

In most of the column systems studied, Columbia* LC carbon was used as the adsorbent because this material had been thoroughly tested in earlier batch-type studies[1] and thus provided a logical starting point for extension of the present investigations to column-type operation. Activated carbon obtained from the Pittsburgh Chemical Co. was also used in several of the studies to provide some basis for comparison of different types of carbon.

A number of column studies were also carried out with an activated aluminum oxide ("regular-iron" Porocel from Minerals and Chemicals Philipp Corp.). This material was found, however, to be less effective than either of the two types of activated carbon.

Before use, each adsorbent was separated into uniform particle sizes by thorough sieving; portions of suitable size range were then washed in distilled water to remove leachable impurities and adherent powder and were next dried at 105°C. The size chosen for most extensive study consisted of particles passing a United States Standard

* Mention of commercial products does not imply endorsement by the Federal Water Pollution Control Administration.

Sieve No. 50 and retained on a No. 60; the mean particle diameter for this size range is 0.273 millimeters.

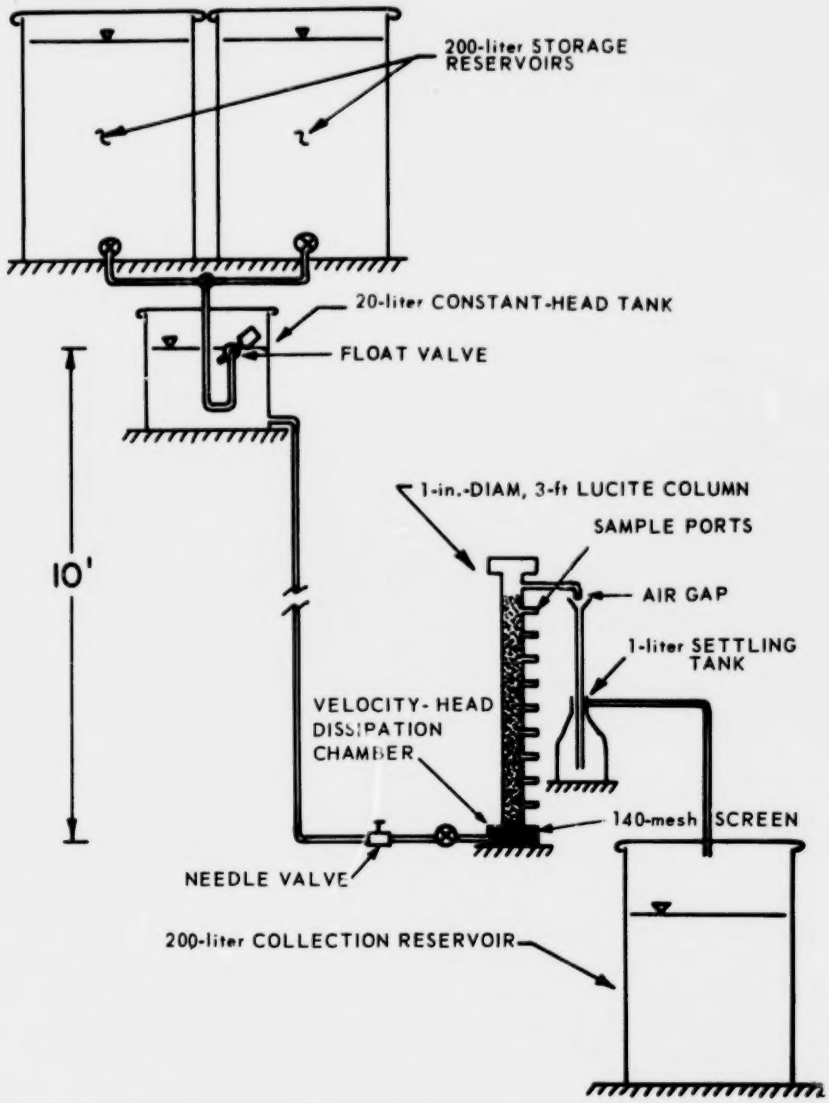

Figure 1. Schematic diagram of experimental apparatus.

The adsorbates used in these studies included a 92.9 percent active material, dodecylbenzenesulfonate, obtained from the Petrochemical Department of the Continental Oil Company; a similar material, Ultrawet D.S., obtained from the Atlantic Refining Company; and Ultrawet K, a branched-chain sulfonated alkylbenzene obtained as a 93 percent active material sodium salt from the Atlantic Refining Co. The first two materials were found to have a molecular weight of 372, and the Ultrawet K, 396.

Other solutes studied included nonylphenoxypolyethoxyethanol (a nonionic surfactant); 2-sec-butyl-4, 6-dinitrophenol (an herbicide-insecticide); phenyl-N, N-dimethylphosphorodiamidate (an insecticide); and 2,4-dichlorophenoxyacetic acid (an herbicide). These substances were obtained from the Dow Chemical Company. Other adsorbates included sodium dodecylsulfate, a Matheson, Coleman, and Bell product, which was better than 95 percent dodecylsulfate and 99.5 percent total alkyl sulfate by analysis; triethanolamine; quinine sulfate; phenol; 2, 4-dichlorophenol; and sodium p-toluenesulfonate, which were obtained as reagent-grade products from Eastman Organic Chemicals.

The adsorbents and the adsorbates were prepared for the studies according to procedures detailed in a previous report in this series.[1]

ANALYTICAL METHODS

Ultraviolet absorption[19] was used for determination of the concentration of the sulfonated alkylbenzene, Ultrawet K, in experiments in which this solute was the only adsorbate present in solution. When this substance was a component of solutions in which other solutes caused interference with the ultraviolet method, the Longwell and Maniece modification of the Jones method using methylene blue was employed.[20] Ultraviolet absorption as previously described[19] was used also for determination of p-toluenesulfonate.

Many of the other substances could also be determined readily by light absorption in the visible or ultraviolet region. Quinine exhibits a maximum in light absorption at 330 millimicrons with a molar absorptivity of 4.70×10^6 square centimeters per mol; 2,4-dichlorophenol has a maximum in absorption at 284 millimicrons with a molar absorptivity of 2.05×10^6 square centimeters per mol; and 2-sec-butyl-4, 6-dinitrophenol (DNOSBP) has a maximum at 375 millimicrons with a molar absorptivity of 13.80×10^6 square centimeters per mol. The absorption of each of these substances was found to follow the Beer-Lambert law for the range of concentrations studied. Thus measurements of absorbance at the indicated wavelengths permitted rapid and accurate determination of the corresponding substances.

The remaining solutes were used solely as components of complex mixtures of organic compounds, and determinations of their individual concentrations were not made. Effectiveness of adsorption in experiments with complex mixtures was evaluated in terms of the overall removal of organic pollutants, which was measured in terms of organic carbon. Determinations of organic carbon were made according to the wet oxidation technique.[21]

EXPERIMENTAL METHOD

An accurately weighed quantity of carbon, usually 45 grams, was mixed well with approximately 1 liter of distilled water, and the mixture was introduced into the adsorption tube. The column was set in place in

the experimental apparatus as shown in Figure 1. Distilled water was run through the apparatus and the column to permit adjustment of flow to the desired rate with the needle valve. The gate valve immediately following the needle valve in the flow train was then closed, the carbon was allowed to settle, and the water in the column was drawn down through a sample port to a level approximately one-fourth of an inch above that of the settled carbon. The distilled water was drained from the remainder of the system. The feed solution was then made up in the storage reservoirs and introduced to the constant-head tank. The gate valve was opened, the carbon expanded, and samples taken at appropriate intervals after displacement of the initial volume of distilled water remaining in the column at the beginning of the run. In addition to "instantaneous" sampling, samples of the total effluent were taken at appropriate intervals of time after initiation of the run. Instantaneous samples were taken at selected ports along the length of the expended column of adsorbent as well as from its top.

Temperature control internal to the system was deemed unnecessary in those studies in which the effect of temperature was not being specifically investigated because the room temperature, and consequently the temperature of the feed solution, varied but little from approximately 28° to 30°C. On the basis of temperature effects noted in batch systems,[1] this slight variation was thought to have no significant effect on the results of the column studies.

Results

Eighteen different column runs were carried out, including three with activated aluminum oxide, two with packed beds of carbon, and one with a 2-inch column.

ACTIVATED ALUMINUM OXIDE

The activated aluminum oxide used in the column studies was a "regular-iron" Porocel obtained from Minerals and Chemicals Philipp Corporation. This material differed considerably in its adsorptive properties and physical behavior from a "low-iron" Porocel used in earlier batch studies.[22] The "regular-iron" Porocel exhibited poor adsorptive characteristics relative to the carbons tested, and in addition, created considerable operational difficulty because it tended to disintegrate and form fine suspensions in water when subjected to the slightest agitation. This tendency was so great that it was impossible to pre-wash the material with any success and to stop continual carryover of colloidal aluminum oxide in the effluent from the columns during experiments. The bauxite tended, furthermore, to agglomerate and be lifted in slugs rather than as free, discreet particles during upflow operation.

The results of the three runs with bauxite columns may be summarized very briefly. All studies were carried out in 1-inch columns,

with 150 grams of activated aluminum oxide in each; the adsorbate in each case was technical alkylbenzenesulfonate in an initial concentration of approximately 60 micromoles per liter (22.4 mg/liter). The first experiment was conducted with 0.273-millimeter bauxite and a flow rate of approximately 2.5 gallons per minute per square foot; the initial portion of effluent from this column had a residual concentration equal to about 80 percent of that of the influent, and after 3 hours the concentration in the effluent had reached over 90 percent of that in the influent. After 25 hours a considerable quantity (approximately 10 to 20%) of the adsorbent had been carried out of the column into the effluent, and the remaining material had begun to agglomerate into relatively large cylindrical masses within the column, rendering maintenance of the rate of flow extremely difficult; at this point the run was terminated.

To provide for more rapid removal of adsorbate from the solution passing through the expanded adsorbent, very fine bauxite, passing a U.S. No. 140 sieve, was used in a second experiment. This material became agglutinated very soon after initiation of the run, forming masses that were forced up the column by the ascending stream of influent. Even as these slugs of material were broken up by vigorous tapping along the walls of the Lucite tube, new slugs formed below them in the column. The experiment had, therefore, to be stopped shortly after its initiation.

A third study in which an intermediate-size bauxite, 0.200 millimeter, was employed failed for the same reasons as did that in which very fine material was used. Collection of valid data on the effluent from either of the latter columns was impossible.

ACTIVATED CARBON

Thirteen fluidized-bed studies were conducted with activated carbon. Columbia LC carbon was used in 10, and 3 were carried out with Pittsburgh carbon. The salient properties of all 13 experimental columns are listed in Table 1. The three columns in which Pittsburgh carbon was used are designated K, L, and M. With the exception of M, which was a 2-inch-diameter column, the columns were 1 inch in diameter. Four experiments were conducted to study the effects of flow rate (columns A to D), and five, to determine effects of particle size (columns E to I).

Typical data for the fluidized-carbon experiments are shown in Figures 2 and 3. The data for column study C, in which the highest flow rate was used, are shown in Figure 2, and those for the experiment in which the lowest flow rate was used, column study D, are shown in Figure 3. In Figures 4 to 6, summaries of effluent concentrations as a function of time are shown for the flow rate studies, for the particle size studies, and for the remainder of the fluidized-column experiments, respectively.

A few experiments were continued until the concentration of solute in the effluent was equal to that in the influent, although the extended

Table 1. PROPERTIES OF EXPERIMENTAL FLUIDIZED-CARBON COLUMNS

Column	Particle size, mm	Total weight of carbon, g	Concentration of adsorbate in influent, μmol/liter	Flow rate, gpm/ft^2	Column height cm, Unexpanded	Column height cm, Expanded
A	0.273	45	67.0	2.75	21	42
B	0.273	45	65.0	1.43	20	30
C	0.273	45	68.4	6.14	22	67
D	0.273	45	69.4	0.68	21	26
E	0.178	45	76.1	2.56	22	60
F	0.503	45	78.5	2.52	18	23
G	0.359	45	78.5	2.58	19	28
H	0.230	45	74.9	2.52	22	41
I	0.273	45	71.7	2.58	21	40
J	0.126	45	59.9	0.68	15	31
K	0.359	50	72.4	2.68	26	37
L	0.200	61	79.7	2.55	29	55
M	1.545	500	80.4	5.12	57	57

curves are not shown in the summary plots. Complete breakthrough in Column I, for example, occurred after about 325 hours.

The columns used in experiments A and I were made nearly identical to check reproducibility of the experimental data; the results for these runs, shown respectively in Figures 4 and 5, accord rather well with each other.

Two experiments were conducted with unexpanded downflow columns, identical in all other respects to the columns used in experiments G and I, to compare this method of operation with fluidization. Despite the relatively large particle sizes (0.359 mm and 0.273 mm respectively), short columns, and an available head of nearly 10 feet, maintenance of the initial flow rate of approximately 2.5 gallons per minute per square foot was not possible. In both experiments the flow rate had dropped to less than one-half of the initial rate within 24 hours, and to about one-tenth of the initial rate within 30 hours.

The relatively sparse data collected during the packed-column experiments indicate that values of C/C_0 for each of these columns were less than 0.1 throughout the 30 hours of operation; these data are for rapidly decreasing flow rates, however, and may not be compared with those for the constant-rate experiments with columns of fluidized carbon. The packed-column experiments serve to underscore the advantage of much smaller headlosses afforded by fluidization.

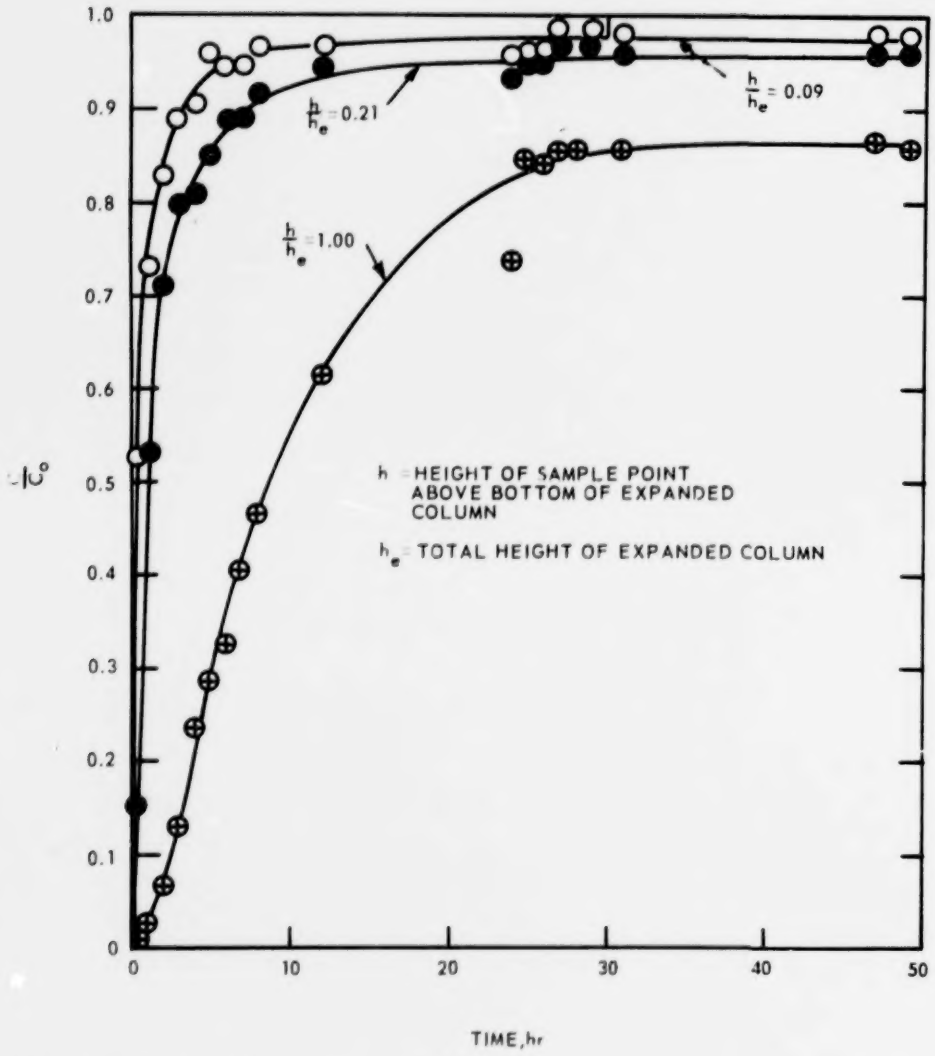

Figure 2. Ratio of concentration at points in fluidized column to influent concentration as a function of time. Column C, 45-g, 0.273-mm Columbia carbon; flow rate = 121.5 ml/min; face velocity = 24.4 cm/min; unexpanded height = 22 cm; expanded height = 67 cm.

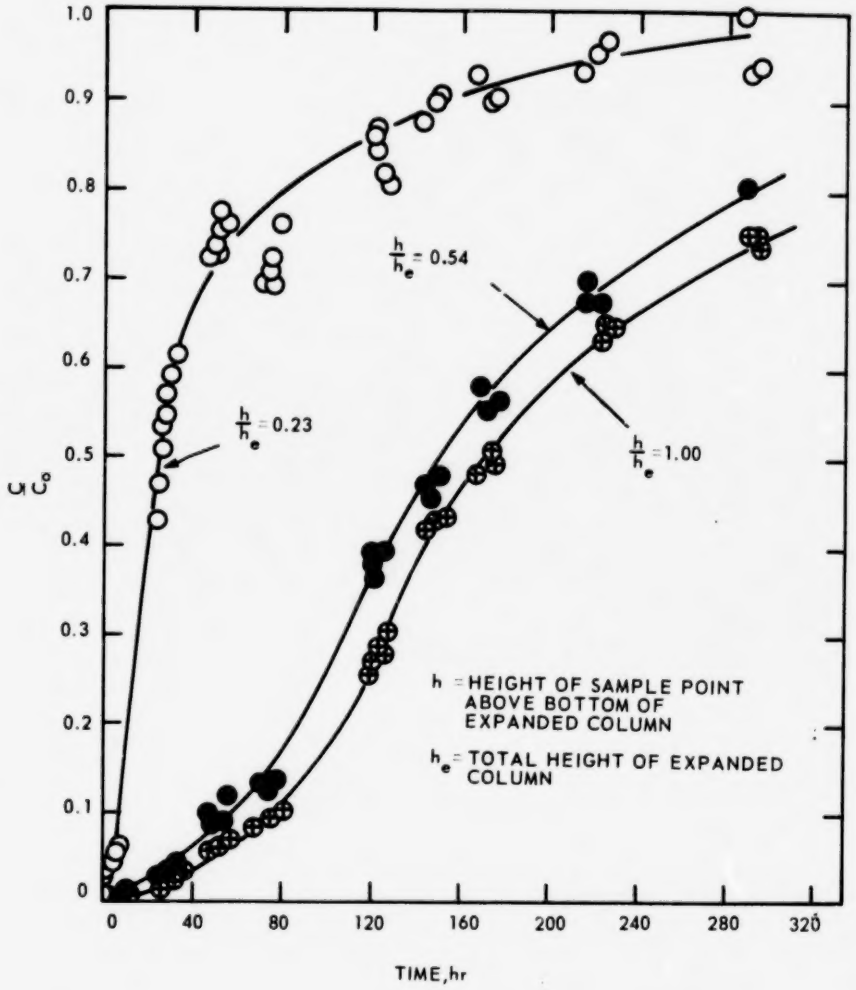

Figure 3. Ratio of concentration at points in fluidized column to influent concentration as a function of time. Column D, 45-g, 0.273-mm Columbia carbon; flow rate = 13.5 ml/min; face velocity = 2.7 cm/min; unexpanded height = 21 cm; expanded height = 26 cm.

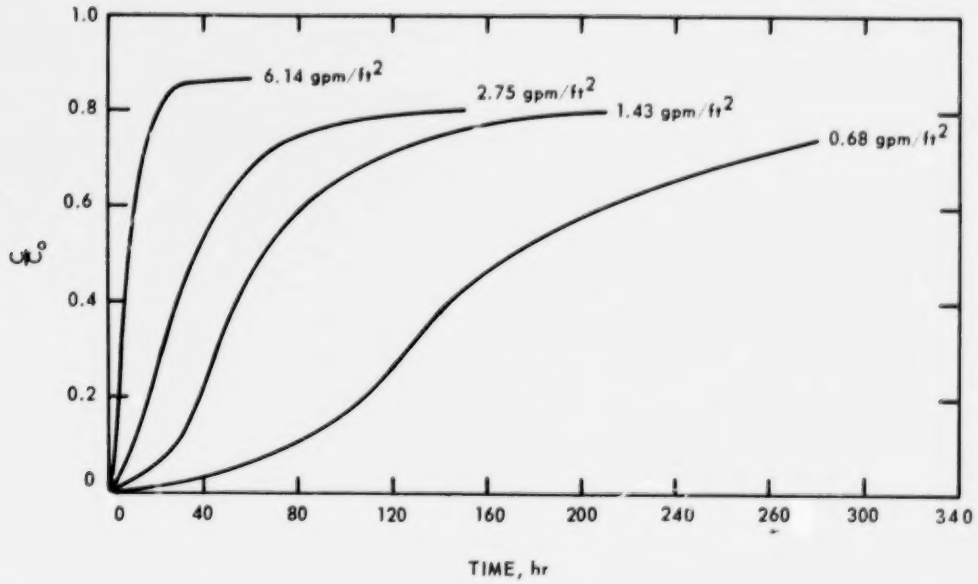

Figure 4. Ratio of effluent concentration to influent concentration as a function of time for different flow rates, 45-g 0.273-mm Columbia carbon.

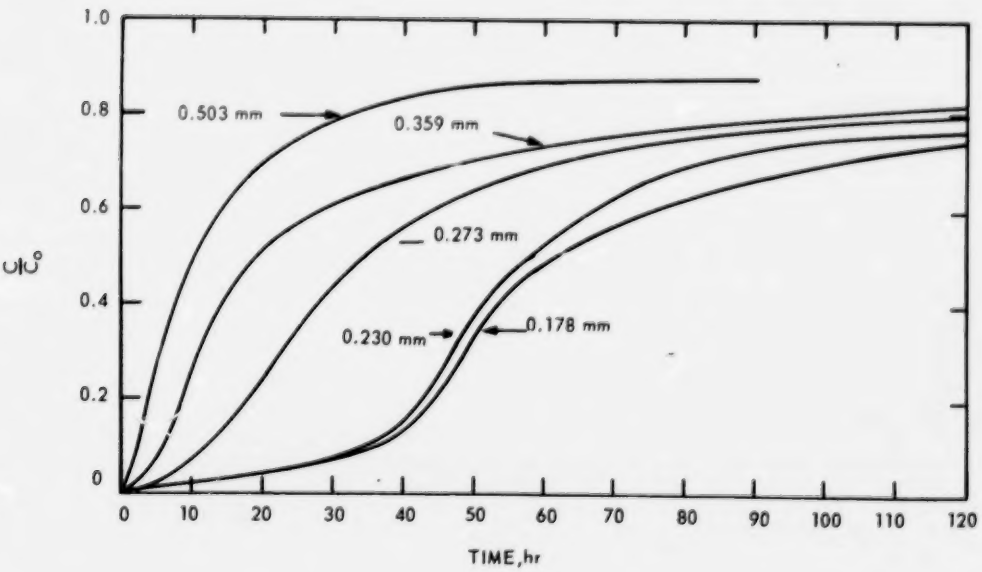

Figure 5. Ratio of effluent concentration to influent concentration as a function of time for different particle sizes of adsorbent, 45-g Columbia carbon, flow rate = 2.5 gpm/ft².

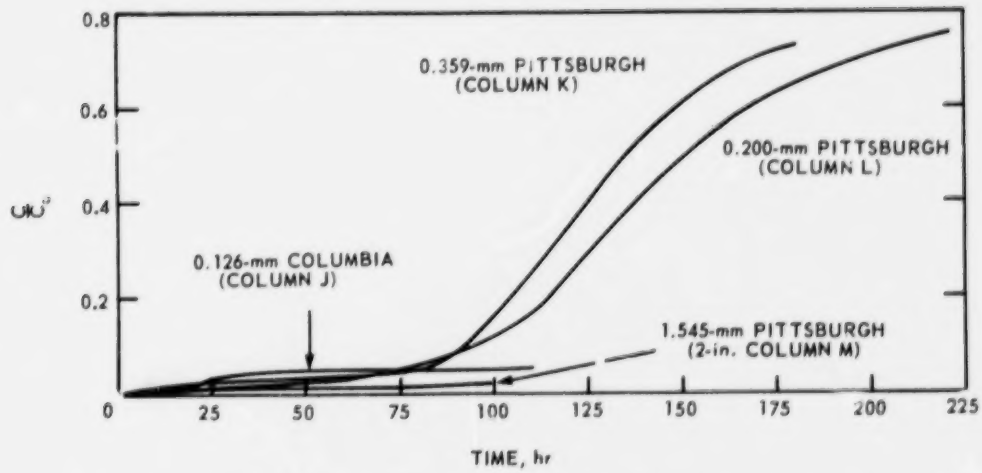

Figure 6. Ratio of effluent concentration to influent concentration as a function of time for additional column studies.

SOLUTE EFFECTS

Previous experiments on adsorption by carbon in fluidized columns had been conducted with highly branched sulfonated alkylbenzenes. It was of interest to explore possible differences in adsorption pattern for different solutes upon passage through fluidized-carbon columns and ascertain whether observed differences can be correlated with characteristics found through more readily accomplished measurements on batch systems. Hence, in one experiment, parallel-columns were run on two solutes with considerably different molecular weights but of the same chemical class of compound. The solutes used were Ultrawet K and sodium p-toluenesulfonate. The latter is the simplest alkylbenzenesulfonate, with a molecular weight of 171 for the anion; the former is a branched-chain alkylbenzenesulfonate with about 15 carbon atoms in the alkyl group.

One reason for the choice of these two solutes was that rates of adsorption and capacities for adsorption on activated carbon from solute solution have been studied previously for p-toluenesulfonate and for materials very similar to the Ultrawet K in batch-type systems, and marked differences in these adsorption characteristics have been observed.[1]

Figure 7 presents data for the adsorption of Ultrawet K from a solution with an initial concentration of 73.3 micromoles per liter in a column containing 45 grams of 0.273-millimeter Columbia carbon; this quantity of the 0.273-millimeter carbon had an unexpanded column height of approximately 22 centimeters. The flow rate for the study was 2.5 gpm per square foot. The form of the curve representing the relative effluent concentration C/C_0 as a function of time is similar to that obtained previously for other highly branched sulfonated alkylbenzenes under similar experimental conditions.[1]

In Figure 8, the curve shown in Figure 7 for Ultrawet K is compared with a similar curve for sodium p-toluenesulfonate. The initial concentration of p-toluenesulfonate in the solution used for this experiment was 79.6 micromoles per liter; carbon size and quantity as well as flow rate were identical to the experiment with Ultrawet K.

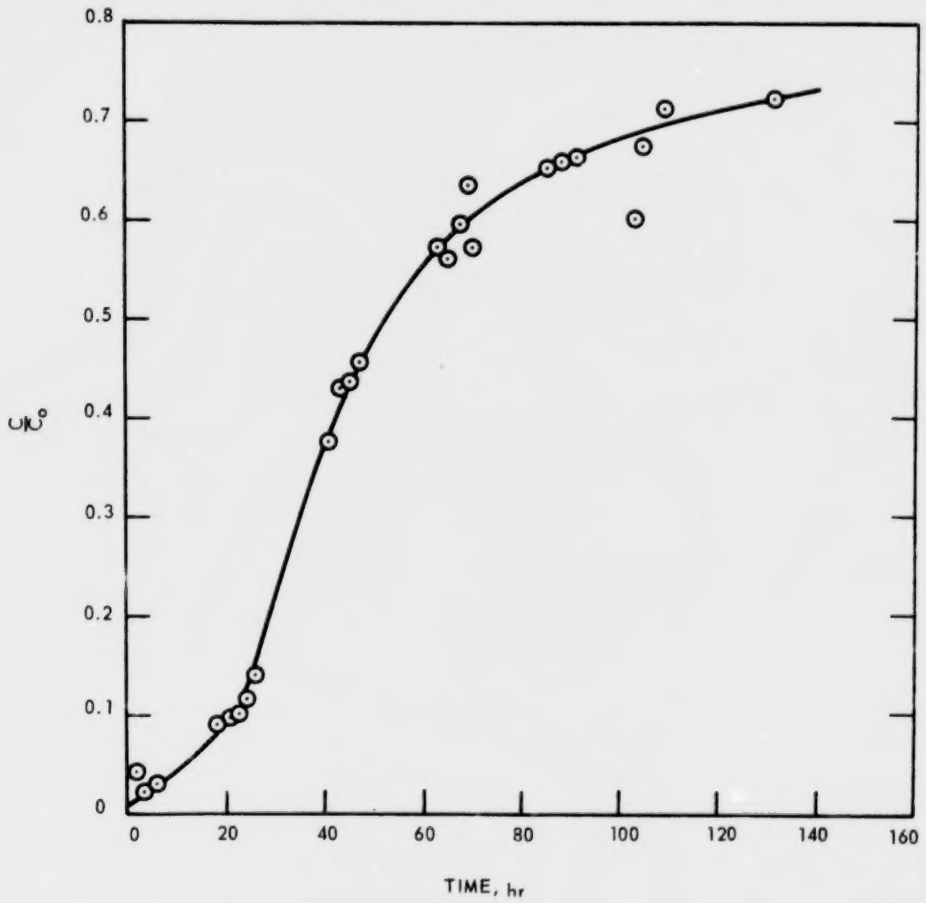

Figure 7. Breakthrough curve for branched-chain sulfonated alkylbenzene (ABS).

Several points of comparison should be noted. First, there was an initial leakage of p-toluenesulfonate considerably greater than that for the ABS, the leakage of the p-toluenesulfonate being 6 percent of its influent concentration to about 2 percent for the ABS. Second, the effluent leakage for the p-toluenesulfonate increased very little for the first 20 hours of operation whereas that for the ABS increased almost from the start and after 16 hours of operation became greater than the leakage from the p-toluenesulfonate column. Third, as a corollary to the second point, the total breakthrough of p-toluenesulfonate was much sharper than that of the ABS. After about 60 hours, the uptake from the ABS solution was once again more effective than that from the p-toluenesulfonate solution. Fourth, after about 100 hours the total integrated uptake from the two solutions had been about the same, but about one-third of the influent ABS was still being removed whereas the capacity of adsorption of p-toluenesulfonate had apparently been exhausted.

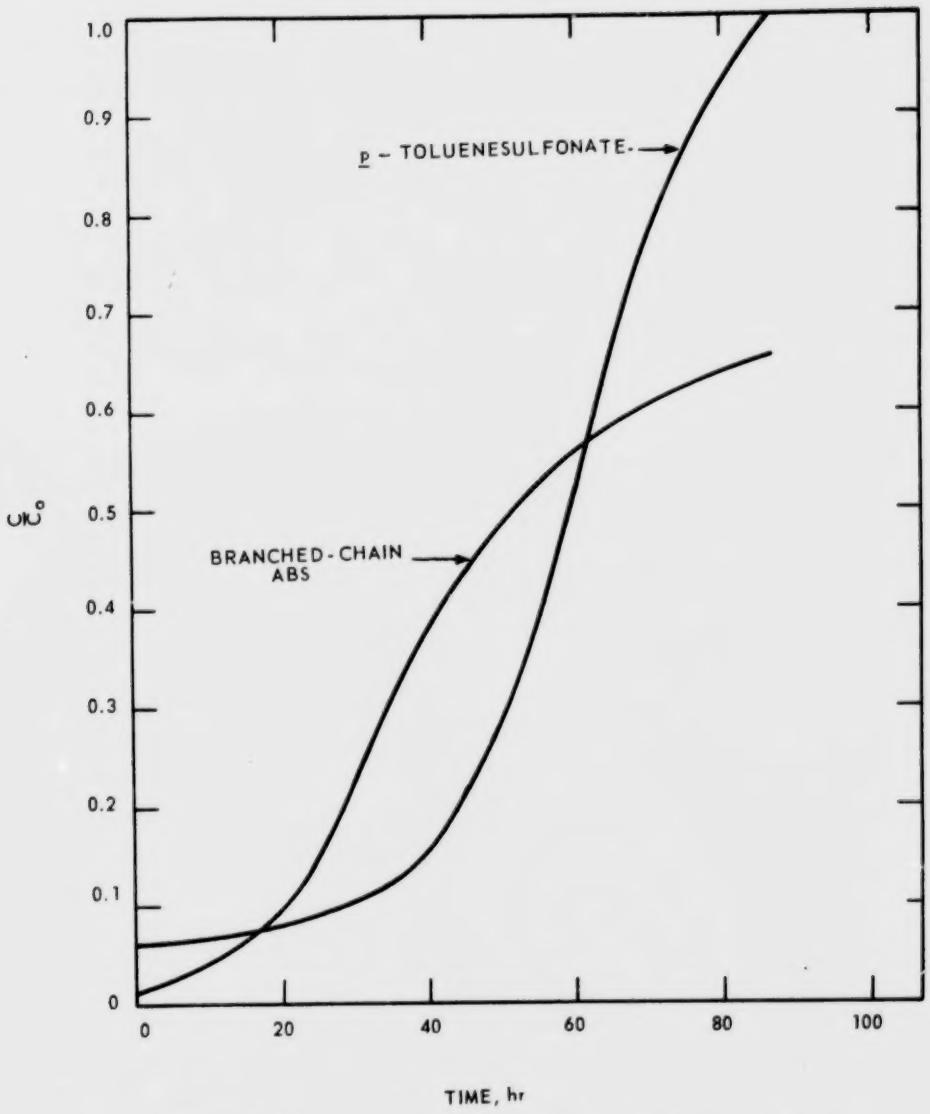

Figure 8. Breakthrough curves for ABS and p-toluenesulfonate.

The fact that the Ultrawet K is taken up more completely during the very early stages of the run than the p-toluenesulfonate is in accord with the findings of previous equilibrium studies in batch systems. During the first few hours of the experiments, the concentration of each solute in the water passing up through the expanded bed of fresh carbon is reduced to a low figure beyond the first few inches of the column. Previous investigations of the equilibria of adsorption on carbon have indicated that the energy of adsorption for a high-molecular-weight sulfonated alkylbenzene is greater than that for p-toluenesulfonate.[1] In other words, effective adsorption is observed for much smaller concentrations with the ABS than with p-toluenesulfonate. Thus, removal by

adsorption of the last traces of the high-molecular-weight Ultrawet K should be considerably easier than complete cleanup of the p-toluenesulfonate.

The increasing leakage of the ABS in contrast to that of the p-toluenesulfonate over the first 20 hours of column operation can be associated with the relative rates of adsorption observed in batch studies on these solutes. Because of the slow rate of penetration of the ABS into the interior surfaces of the carbon granules, the active external points soon reach a significant fraction of saturation, and subsequent adsorption is less rapidly effective. With the p-toluenesulfonate a relatively rapid migration of adsorbed material to the interior permits renewal of active external surface and substantial maintenance of efficiency of adsorption for a longer period. When nearly full capacity has been attained, a relatively sharp breakthrough occurs.

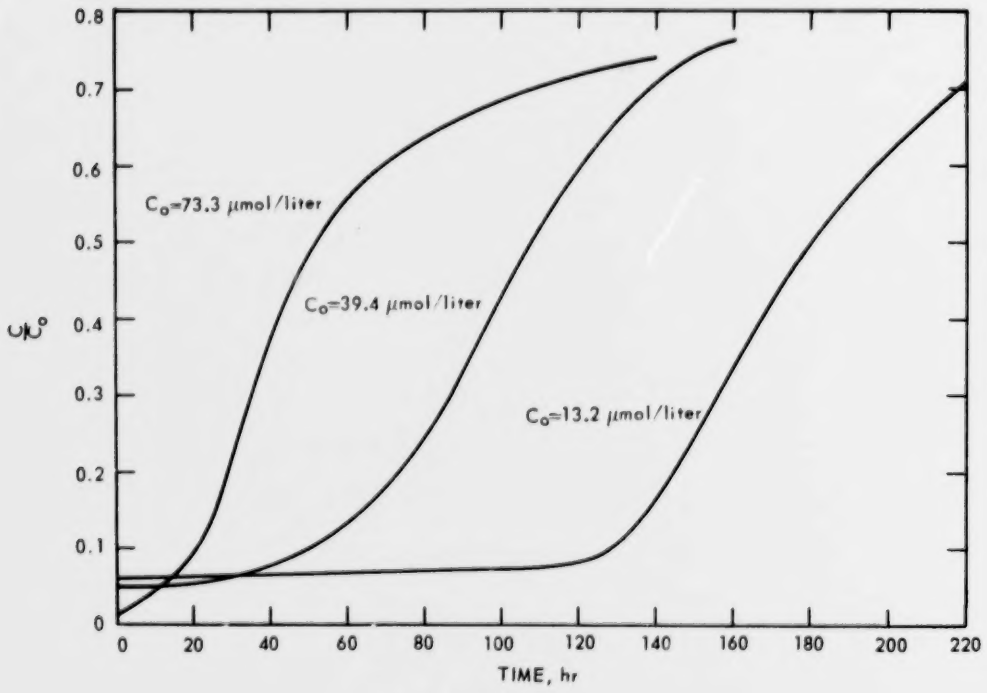

Figure 9. Breakthrough curves for ABS in solutions of different initial concentration.

Maintenance of adsorption capacity in the column adsorbing ABS beyond the time required to exhaust the column adsorbing p-toluenesulfonate is expected on the basis of the greater adsorption capacity for the former material found in the batch equilibrium studies.

The separate-column studies with Ultrawet K and p-toluenesulfonate thus indicate that at least qualitative prediction of column behavior may be possible from knowledge of batch-system behavior, at least for cases in which a single-solute solution is passed through the column.

Figure 9 presents breakthrough curves for three experiments in which the effects of different concentrations of Ultrawet K were studied. The flow rate for each experiment was 2.5 gpm per square foot, and each column contained 45 grams of 0.273-millimeter Columbia carbon.

The effect of concentration on breakthrough of solute is as would be expected, that is, the greater the concentration the more rapid the breakthrough. Note, however, that at the points corresponding to $C/C_o = 0.1$ the total weights of ABS adsorbed were about the same in all three runs. Although leakage appears greater at the smaller influent concentrations, note that the actual effluent concentrations at zero time were 0.85, 1.5, and 0.8 ppm for increasing influent concentrations. Apparently then, initial effluent concentrations at a fixed face velocity will be determined primarily by the depth of the adsorption column rather than by the influent concentration.

One other noteworthy point is that with the lowest influent concentration, 13.2 micromoles per liter or 5.2 milligrams per liter, better than 90 percent adsorption was maintained with just a 9-inch settled depth of carbon for more than 5 days. This would mean about 40 days' effective operation for a 5-foot settled depth with this concentration of material to be removed.

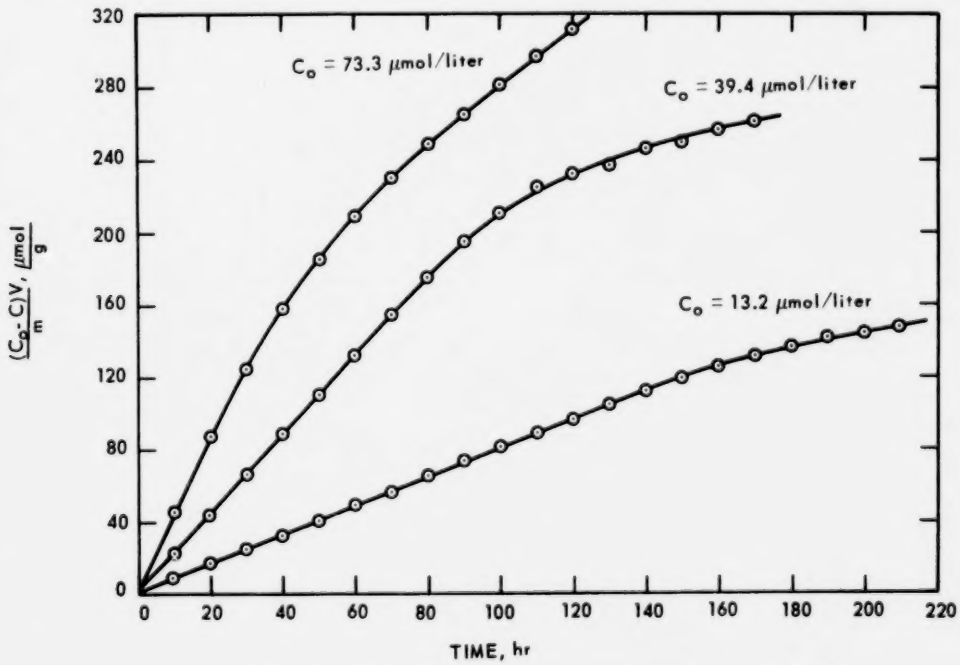

Figure 10. Cumulative adsorption of ABS from solutions of different initial concentrations.

Figure 10 shows total quantity of solute removed from solution by the 45 grams of carbon in each experiment. As would be expected on the

bases of the increased driving force for transfer with increased concentration of solute in solution and of greater capacity of the carbon at the greater influent concentration, both the rate of uptake and total quantity of solute removed are greater at the higher influent concentrations of Ultrawet K for the same period of time. After 100 hours of operation, the carbon in the experiment in which the influent concentration of solute was 73.3 micromoles per liter had removed a total quantity of solute equal to approximately 11 percent of the weight of the adsorbent, and for the experiment with C_0 = 13.2 micromoles per liter, the solute removed was only about 3 percent of the weight of the carbon. Since continuing the experiments at the lower initial concentrations was impractical until the carbon was exhausted, full capacities as a function of concentration could not be measured.

TEMPERATURE EFFECTS

Three experiments were carried out with Ultrawet K as solute at solution temperatures of 36°C, 28°C, and 16°C. Flow rates of 2.5 gpm per square foot were maintained in columns containing 45 grams of 0.273-millimeter Columbia carbon. The initial concentrations of solute were closely the same, in the range of 77 to 80 micromoles per liter. The experiment at 28°C was at room temperature; for the experiment at 16°C the influent was chilled by means of a conventional Freon compressor with the cooling coil immersed in the constant-head tank; a blade-type heater was used in the constant-head tank to heat the influent for the experiment at 36°C. Each temperature given is an average of the temperatures of the influent and effluent for a column. Temperature differences between the influent and effluent for each experiment were less than 3°C.

As shown in Figure 11 little difference was observed in the total uptake of solute as a function of time for any of the temperatures studied. Such a result is to be expected, for the total uptake is primarily a function of the adsorptive capacity of the carbon with beds of sufficient depth and depends very little on the rate of adsorption. Adsorptive capacity does not change greatly over a small temperature range such as that used in these experiments.

The effect of temperature should be noted most significantly for column work in the steepness of the breakthrough portion of the curve of relative effluent concentration as a function of time. At lower temperatures, where the rate of adsorption is less, increasing leakage should begin sooner and a more gradual approach to full saturation should be observed. A close look at the experimental points in Figure 11 reveals an indication of this effect, for the data at 36°C beyond 25 hours lie consistently above the mean curve and more nearly maintain the linear relationship characteristic of complete adsorption, while the data at 18°C lie consistently below the mean curve, indicating increasing leakage through the column.

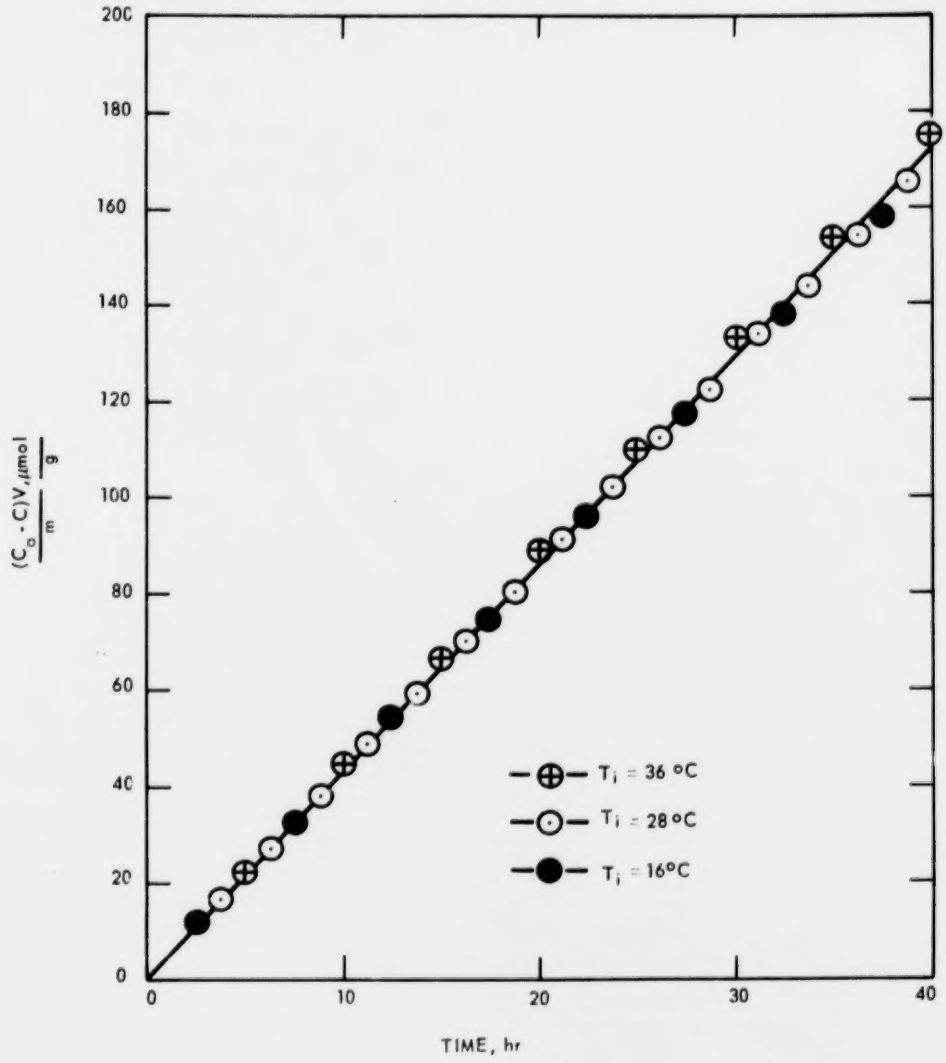

Figure 11. Cumulative adsorption of ABS from solutions at different temperatures.

pH EFFECTS

A preliminary investigation of the effect of solution pH on uptake of solute by carbon in a fluidized bed was made by passing a solution of Ultrawet K, with an unadjusted pH slightly below neutral, at a flow rate of 2.5 gpm per square foot through a column containing 45 grams of 0.359-millimeter Columbia carbon. The larger particle size was used so that more rapid breakthrough would be obtained. When the value of C/C_O for the experiment reached 0.55, the pH of the influent was decreased to 2.5 by addition of concentrated phosphoric acid. As illustrated by the data for this run plotted in Figure 12, the decrease in leakage after this acidification of the influent was dramatic.

To test the effect of solution pH more extensively, four experiments were conducted at different pH values, each with a column containing 45 grams of 0.273-millimeter Columbia carbon and a flow rate of 2.5 gpm per square foot. The initial concentration of solute, Ultrawet K, in each experiment was within the range from 79 to 81 micromoles per liter. Adjustment of pH in the solutions to values of 3.9, 6.6, 7.9, and 10.0, respectively, was accomplished by appropriate addition of phosphoric acid or phosphate. The pH values given are for the influents to the columns.

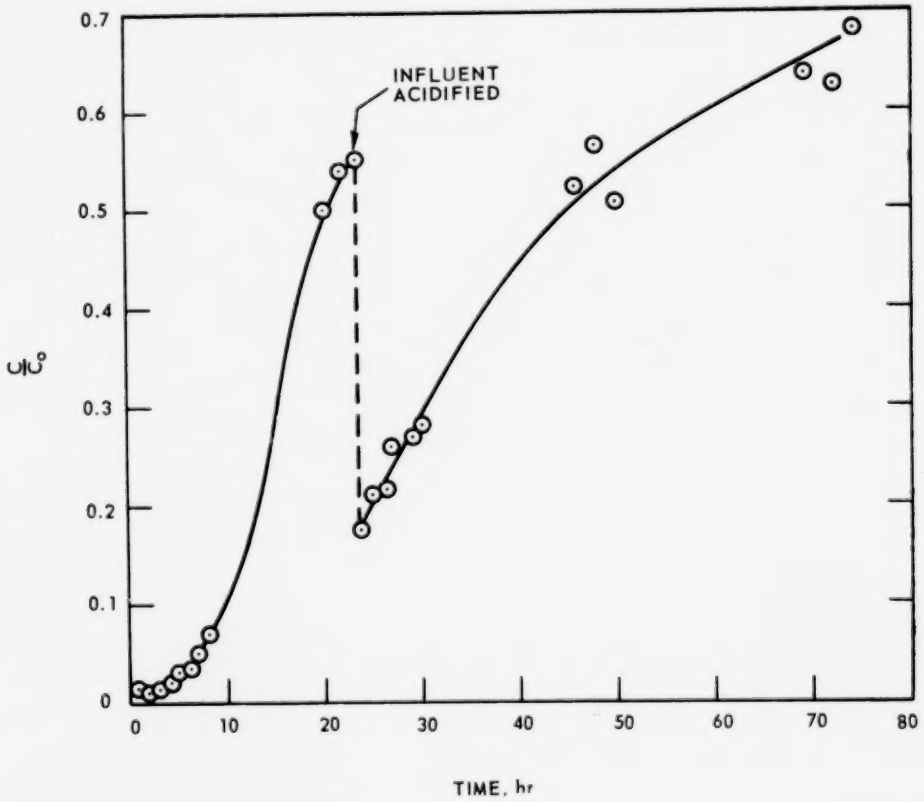

Figure 12. Effect of acidification on the breakthrough curve for ABS.

Data for the pH studies are presented in Figure 13, which shows the total quantities of solute removed from solution by the carbon as a function of time. A notable difference exists between the total amounts of solute removed from solution in the experiments at the highest and lowest pH values tested, the total amount at any time being considerably greater at low pH. The experiments at intermediate pH levels are observed to fit into the pattern of increasing removal with decreasing pH. The observed dependence of solute removal on pH for the column studies accords with previous work in which both rates and final positions of equilibrium for adsorption of sulfonated alkylbenzenes on the experimental carbon in batch-type systems were found to increase with decreasing pH.[1]

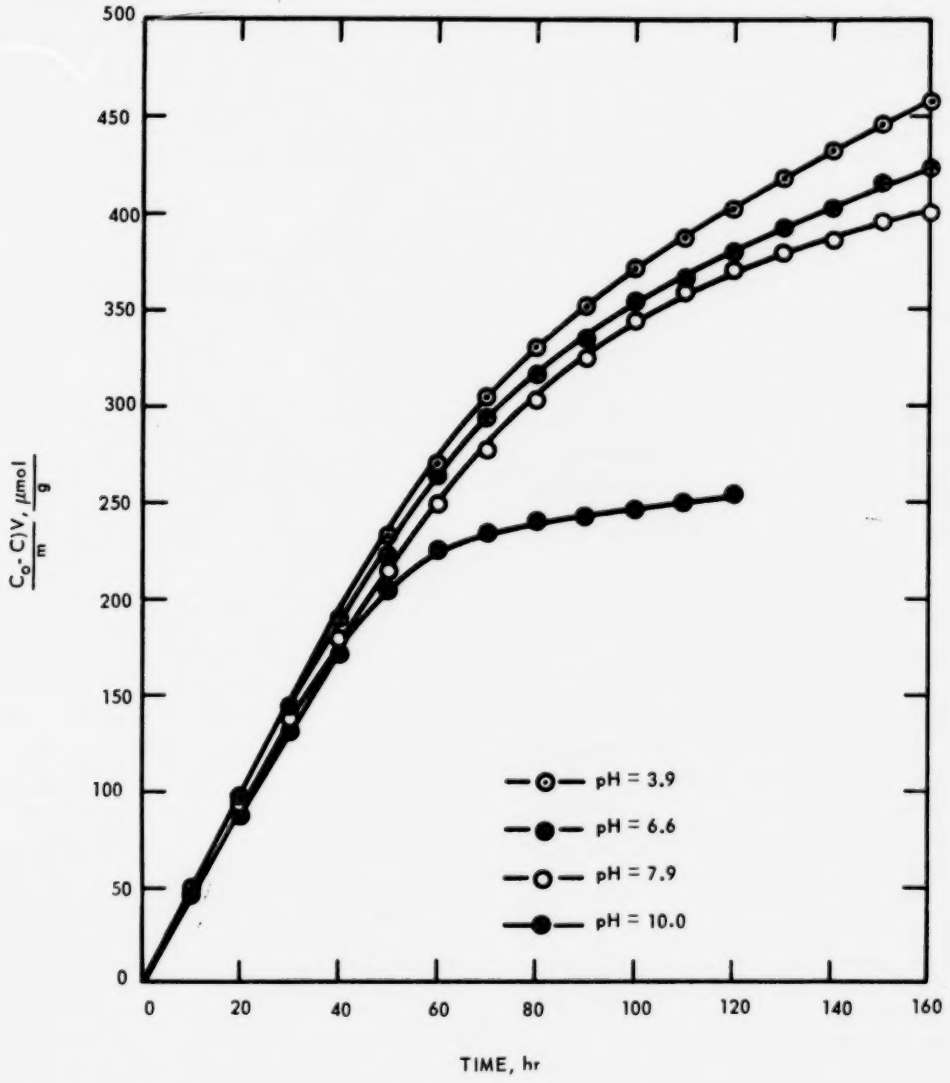

Figure 13. Cumulative adsorption of ABS from solutions at different pH values.

Even so, in order to show marked changes in adsorption with pH, use of very high or low pH values was necessary. Over the pH range of particular interest, 6 to 8, differences in adsorption efficiency were minor. More pronounced effects may be obtained with other types of pollutants, but in general it can be expected that normal pH variations will not affect significantly the operation of activated-carbon columns.

MULTICOMPONENT SOLUTIONS

That solutes in multiple-component solutions compete with one another for adsorption on carbon has been demonstrated for agitated nonflow systems.[23] Studies have been carried out during the present investigation to explore the nature and extent of competitive interactions

in continuous-flow systems. These studies are significant for evaluation of the suitability of continuous-flow adsorption systems for waste-water treatment because the waste water to be treated rarely contains but one organic pollutant. Rather, waste waters are likely to be heterogeneous mixtures of complex organic substances of different chemical types or classes.

In these investigations, solute mixtures of two, three, four, and eight components have been studied.

Two Components

Some pronounced effects of sodium dodecylsulfate on the adsorption of a sulfonated alkylbenzene in batch systems have been noted previously.[23] Hence, mixtures of sodium dodecylsulfate and the branched sulfonated alkylbenzene, Ultrawet K, were employed as solute in initial studies of adsorptive competition on columns.

A solution containing 71.6 micromoles of Ultrawet K per liter and 75.0 micromoles of dodecylsulfate per liter was passed at 2.5 gpm per square foot through a column containing 45 grams of 0.273-millimeter Columbia carbon. Because a simple analytical technique for dodecylsulfate in dilute solution was not available, only the concentration of the ABS was determined in the effluent. Figure 14 presents the breakthrough curve found for the Ultrawet K (ABS) in this study and compares it with a breakthrough curve for a pure solution of the ABS. The experiment with the ABS alone was carried out under conditions identical to those with a solution containing 73.3 micromoles of ABS per liter.

In Figure 14, the presence of the dodecylsulfate apparently has a marked effect on the over-all adsorption of the sulfonated alkylbenzene. The competitive effect appears, however, to be not significant in the early stages of the run; a major difference between the breakthrough curves for ABS in mixed and pure solution is noted only after about 55 hours of operation of the column. During the first 55 hours the carbon apparently had sufficient capacity for both solutes so that little effective competition for adsorption occurred. Since in this experiment the dodecylsulfate was added to the ABS concentration rather than in place of part of it, whatever dodecylsulfate was adsorbed would be expected to reduce the adsorptive capacity for ABS.

Three Components

To test further the effects of solute interactions on adsorption in fluidized columns from solutions containing mixtures of organic compounds, a column study was run with a solution containing three different classes of organic compounds. The influent solution consisted of Ultrawet K at a concentration of 43.6 micromoles per liter, 2-sec-butyl-4, 6-dinitrophenol (DNOSBP) at a concentration of 31.8 micromoles per liter, and quinine sulfate at a concentration of 26.9 micromoles per

liter (as the quinine base). The flow rate for this experiment was 2.5 gpm per square foot and the column consisted of 45 grams of 0.273-millimeter Columbia carbon.

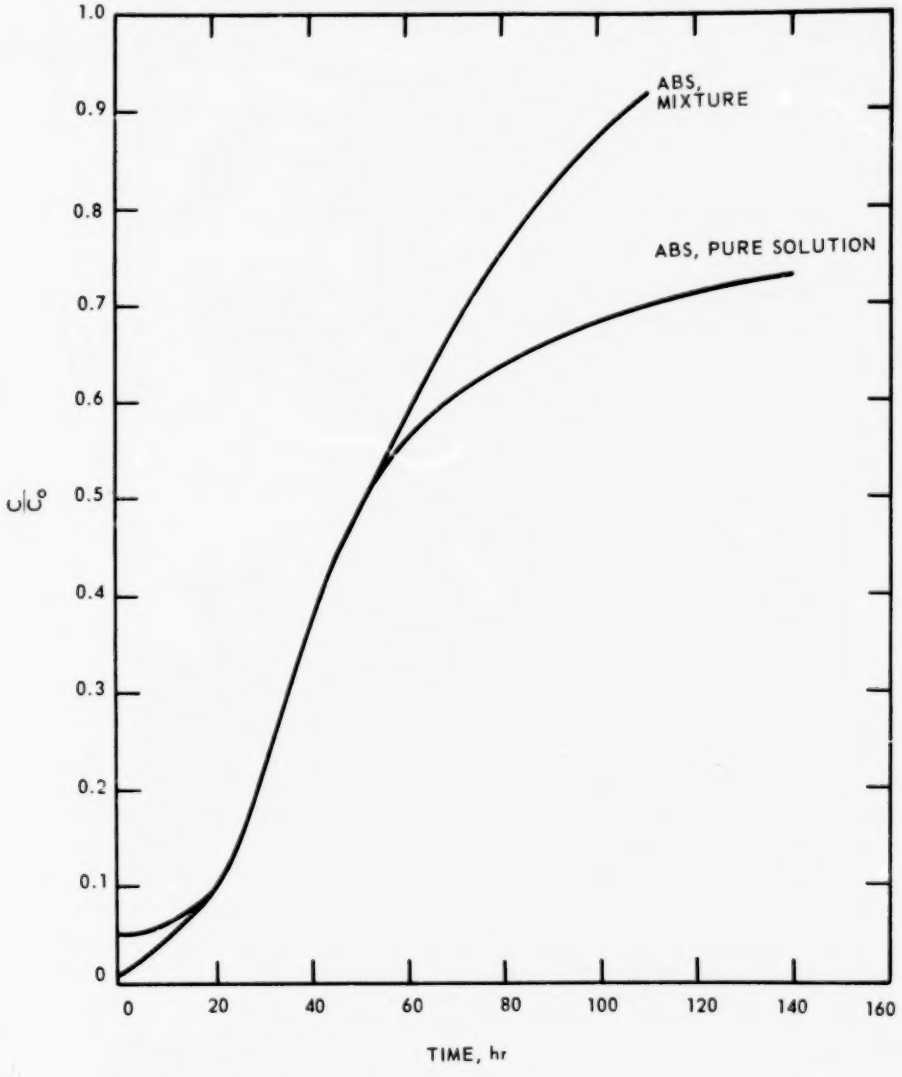

Figure 14. Breakthrough curves for ABS for a single-solute solution and for a bisolute solution with dodecylsulfate

Analyses for concentration of the ABS in the mixed solution were carried out with the methylene blue procedure mentioned previously; no interference from the quinine or the DNOSBP was experienced with this procedure. Determinations of quinine and DNOSBP were made by spectrophotometric measurements at 330 and 375 millimicrons, respectively. The molar absorptivities for these substances at their respective wavelengths for peak adsorption have been listed earlier in this report. At 375 millimicrons the molar absorptivity of the quinine

was 0.07 x 10^6 square centimeters per mole, and that for the DNOSBP at 330 millimicrons was 4.71 x 10^6 square centimeters per mole. Determinations of individual concentrations of these two solutes thus required measurement of each sample at each of the two wavelengths, and simultaneous solution of two absorbance-concentration equations.

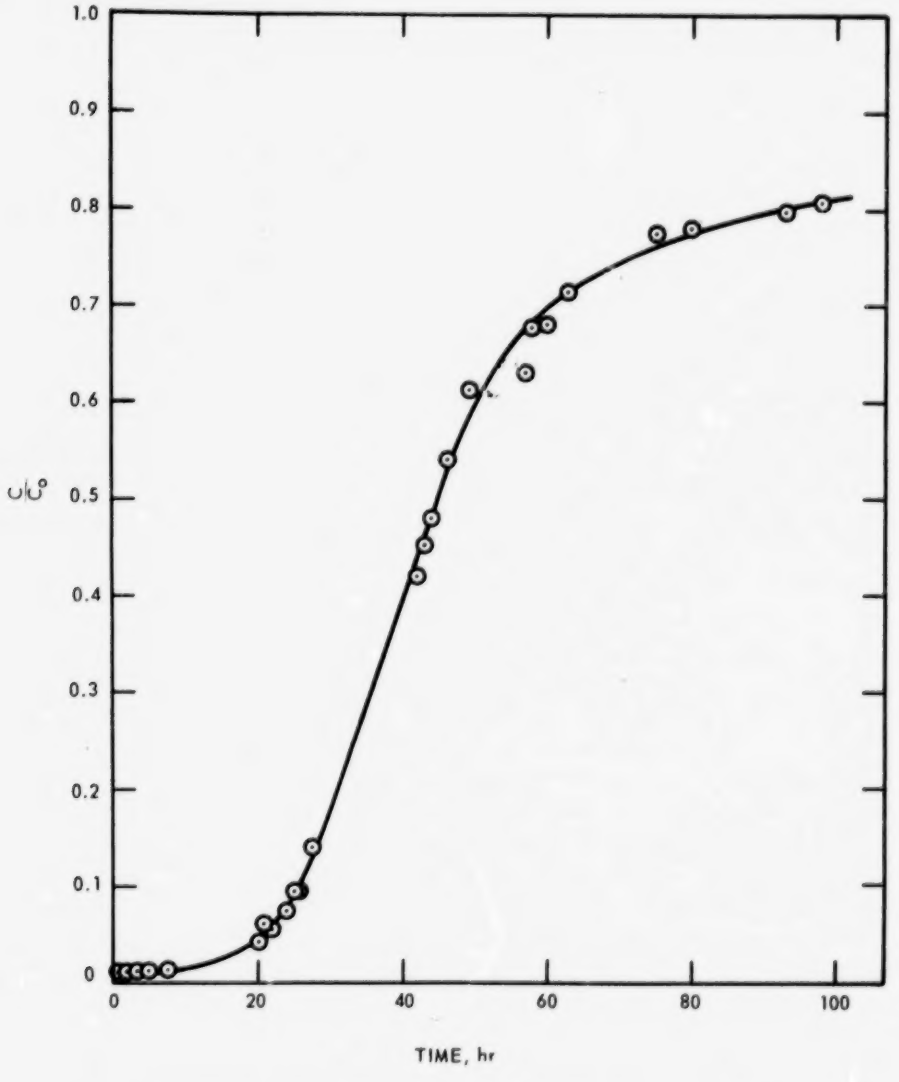

Figure 15. Breakthrough of organic solute with a mixture of ABS, DNOSBP, and quinine.

The overall breakthrough curve for the mixture is shown in Figure 15. The concentration ratio plotted in Figure 15 is for the total concentrations of all the organic solutes present in the solution, computed by summing the results of the individual determinations. The overall breakthrough curve is similar in pattern to those observed previously for single-solute solutions.

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Figure 16 shows breakthrough curves for each of the components of the mixture. The breakthrough for the ABS in the mixture is much more rapid than that for a pure solution of similar initial concentration of ABS is. This fact is illustrated by the curves plotted in Figure 17. The breakthrough curve shown in Figure 17 for the single-solute solution was obtained under identical flow and adsorbent conditions with a 39.4-micromoles-per-liter solution of the Ultrawet K.

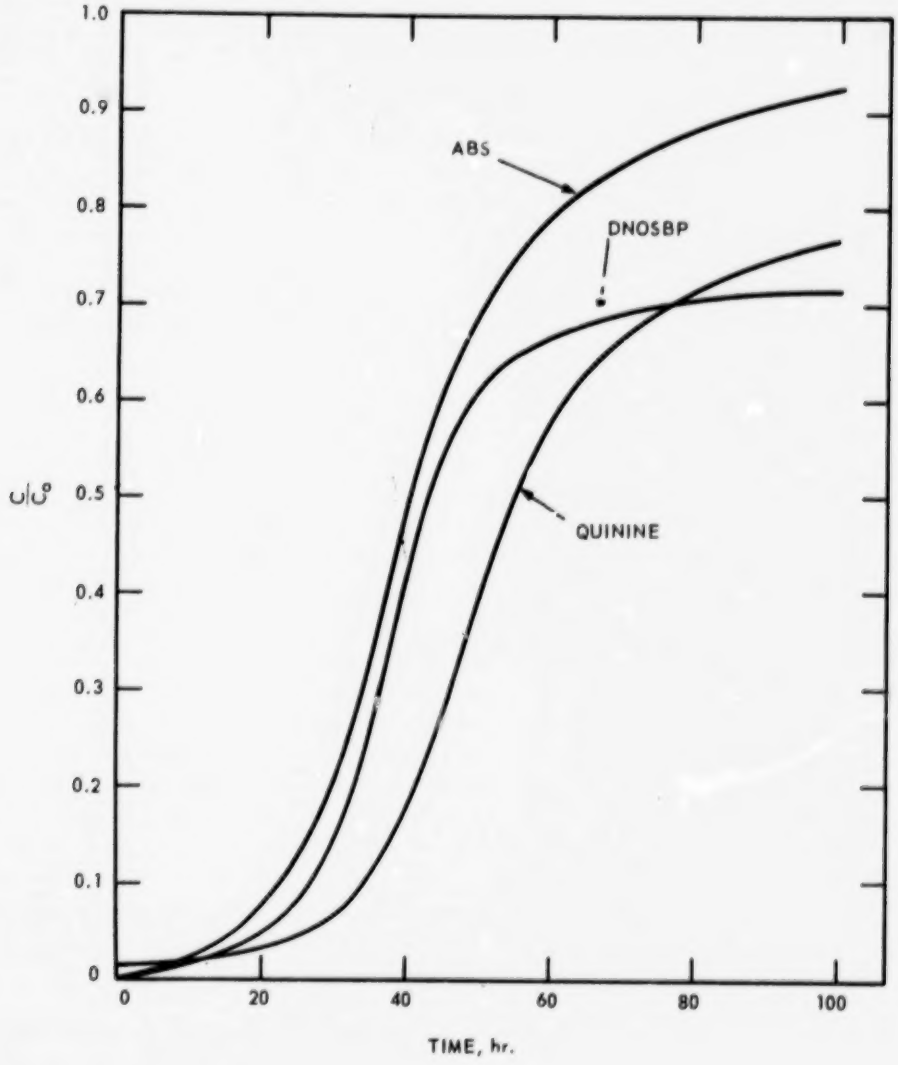


Figure 16. Breakthrough curves for the components with s solute mixture of ABS, DNOSBP, and quinine.

On the other hand the breakthrough is not as rapid as would have been expected for ABS alone at a concentration equal to 102 micromoles per liter, the sum of the component concentrations. In fact the curve is rather similar to that obtained with 73 micromoles of ABS per liter. This tends to indicate some enhancement of total adsorptive capacity for

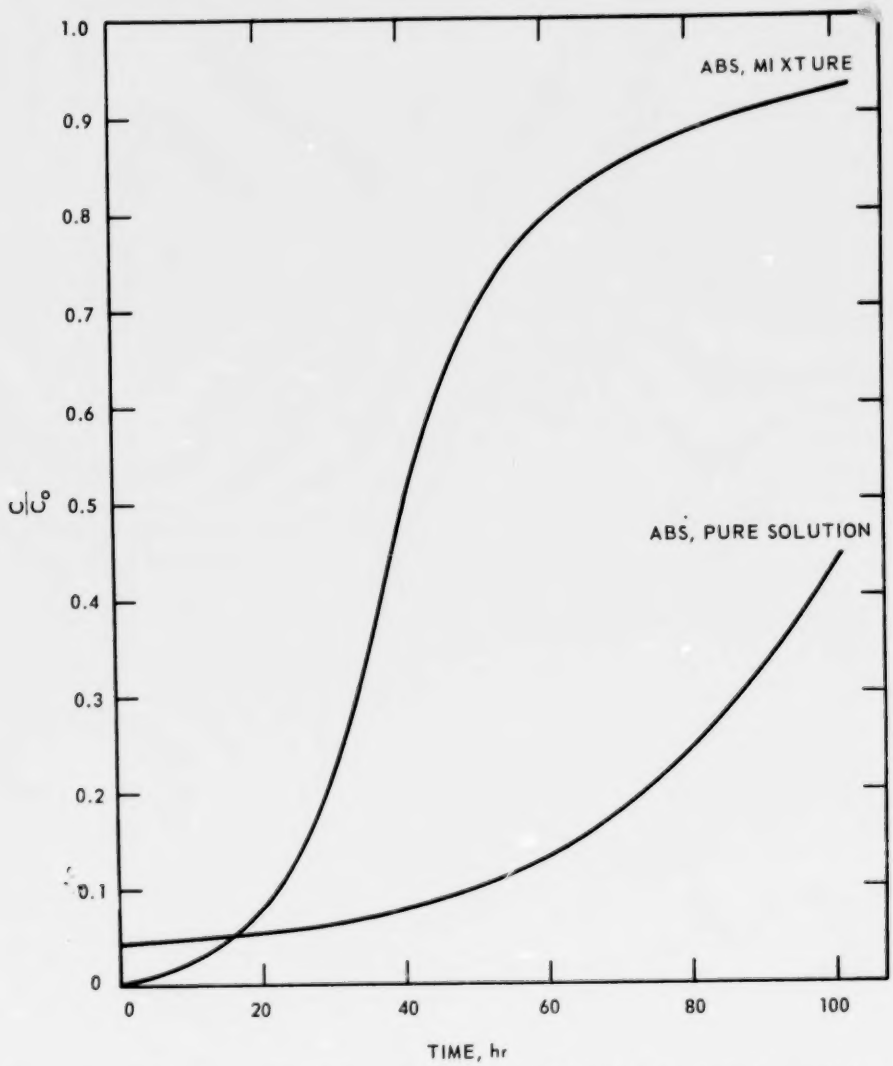


Figure 17. Comparison of breakthrough curves for ABS with a single-solute solution and with a solute mixture with DNOSBP and quinine.

the mixed components, like that found earlier in the batch studies of competitive adsorption.

There were no single-solute column studies for quinine and DNOSBP with which the other curves in Figure 16 might be compared.

The curves shown in Figure 16 do not bring out completely the adsorption picture for this experiment with a multicomponent solution. Figure 16 alone gives the impression that the amount of ABS adsorbed was less than the amount of DNOSBP adsorbed, and that the amount of quinine adsorbed was greatest of all. Actually, because of the initial differences in concentration, the amounts of individual solutes removed from the mixed solution flowing through the column were the reverse of this order. This is shown by the cumulative uptake plots in Figure 18.

Comparison of Figure 18 with Figure 10 shows that the extent of adsorption of the ABS from the mixture was less than that from a pure solution of approximately the same concentration for long periods of operation. For example, the quantity of ABS adsorbed from the mixture after 100 hours was about 130 micromoles per gram of carbon, while for a pure solution of similar initial concentration of ABS, the quantity adsorbed after 100 hours was about 210 micromoles per gram of carbon (Figure 10). The total organic matter adsorbed after 100 hours—the sum of ABS, DNOSBP, and quinine—was, however, 350 micromoles per gram.

In an effort to determine whether the observed adsorption patterns for the mixture could be predicted from batch-system studies, kinetic and equilibrium experiments with nonflow systems were conducted with the same mixture of the three solutes and also with solutions of the three individual components in each of which the initial concentration of solute was the same as its initial concentration in the mixture.

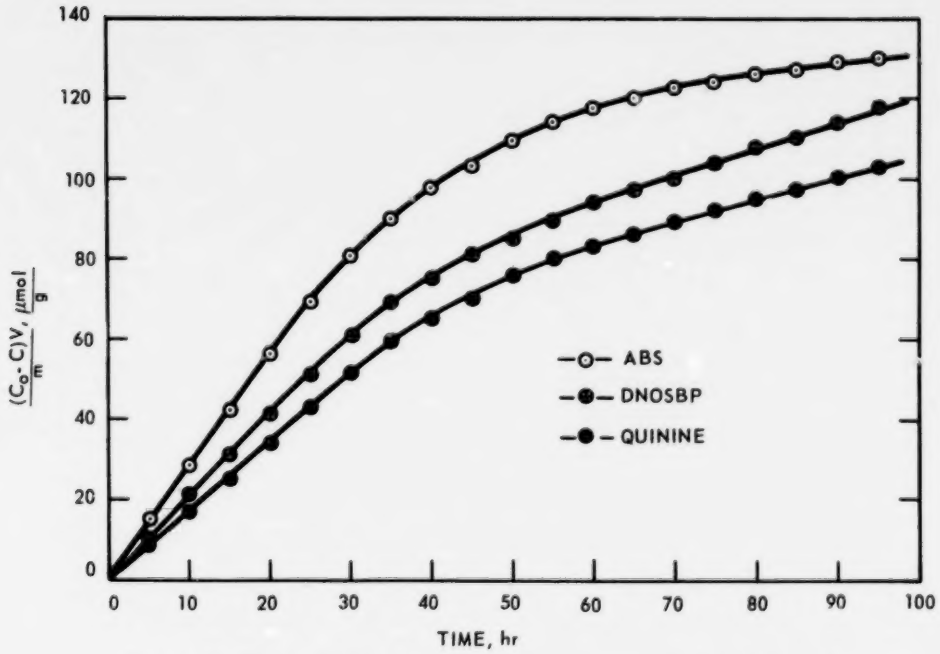


Figure 18. Cumulative adsorption of the components of a mixture of ABS, DNOSBP, and quinine.

Figure 19 shows a plot of data for the rate of adsorption of quinine, obtained from the batch-type experiments. Both the pure solution and the mixture studies were conducted at 29°C. Fifty milligrams of 0.273-millimeter Columbia carbon per liter was used in the experiment with the pure quinine solution, and 250 milligrams of the same carbon per liter was used for the experiment with the multicomponent solution to take account of the difference in total concentration of organic solutes present. The data in

Figure 19 have been linearized for the initial portions of the rate studies by plotting the amount removed from solution as a function of the square root of the time, according to an intraparticle-transport rate step.[1]

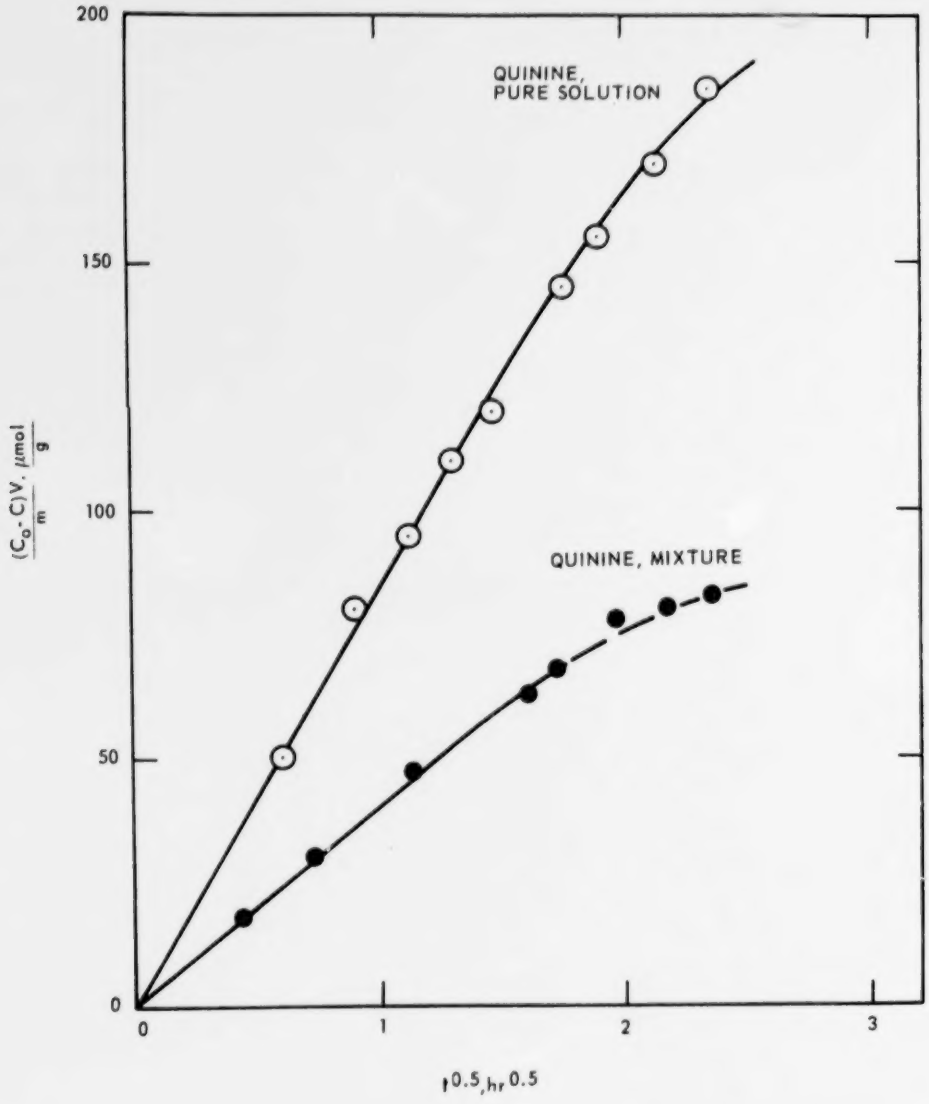


Figure 19. Rates of adsorption of quinine from a single-solute solution and from a mixture of ABS, DNOSBP, and quinine under agitated non-flow conditions.

There is a clear reduction in the rate of uptake of the quinine from the mixture as compared with the rate for the pure solution. Note also, however, that while the amount adsorbed per unit of carbon from the multicomponent solution in an hour was about half that in the pure solution, the mole fraction of quinine in the multicomponent solution was only about 0.23.

Similar data were obtained for the other solutes; rate constants derived from the data are listed in Table 2. The values for the relative rate constant, k, are squares of slopes of plots of the type shown in Figure 19. These data indicate that the rate of adsorption of DNOSBP is by far the most adversely affected in the mixture. There seems to be some tendency for all the rates to reduce to a more nearly common value in the multicomponent solution. This is also indicated by the parallel slopes of the breakthrough curves in Figure 16.

Table 2. RELATIVE RATES OF ADSORPTION FROM PURE SOLUTIONS AND MULTICOMPONENT SOLUTION 0.273-mm COLUMBIA CARBON, AGITATED NONFLOW SYSTEM, 28°C

Solute	Relative rate constant, k, $[(\mu mol/g)^2/hr] \times 10^{-3}$	
	Pure solution	Multicomponent solution[a]
sulfonated alkylbenzene	3.60	1.85
quinine	7.23	1.60
2-sec-butyl-4,6-dinitrophenol	57.60	0.26

[a] Mixture: 43.6 μmol sulfonated alkylbenezene per liter, 26.9 μmol quinine per liter, 31.8 μmol 2-sec-butyl-4,6-dinitrophenol per liter

Table 3. LANGMUIR CONSTANTS FOR ADSORPTION ISOTHERMS; 0.273-mm COLUMBIA CARBON, 30°C;

LANGMUIR EQUATION: $X = \frac{X_m bC}{1+bC}$

Solute	X_m, $(\frac{C_o - C_{eq}}{m})$, $\frac{\mu mol}{g}$	b, $\frac{1}{\mu mol}$
sulfonated alkylbenzene	455	0.478
quinine	605	4.13
2-sec-butyl-4,6-dinitrophenol	1,850	0.174

Isothermal equilibrium studies at 30°C for the individual component solutions were also conducted with 0.273-millimeter Columbia carbon. A plot of the equilibrium adsorption data for quinine is given in Figure 20. The curve fitted to the points in Figure 20 is a calculated Langmuir-type curve; the linearized form is given in Figure 21.

Langmuir constants for all three solutes are listed in Table 3; X is the amount of adsorbed material per gram of carbon, X_m is the limit-

ing value of X for monolayer adsorption according to the Langmuir model, C is the concentration of solute in solution at equilibrium, and b is a constant expressive of the energy of adsorption and equal to the reciprocal of the concentration at which adsorption is equal to $X_m/2$.

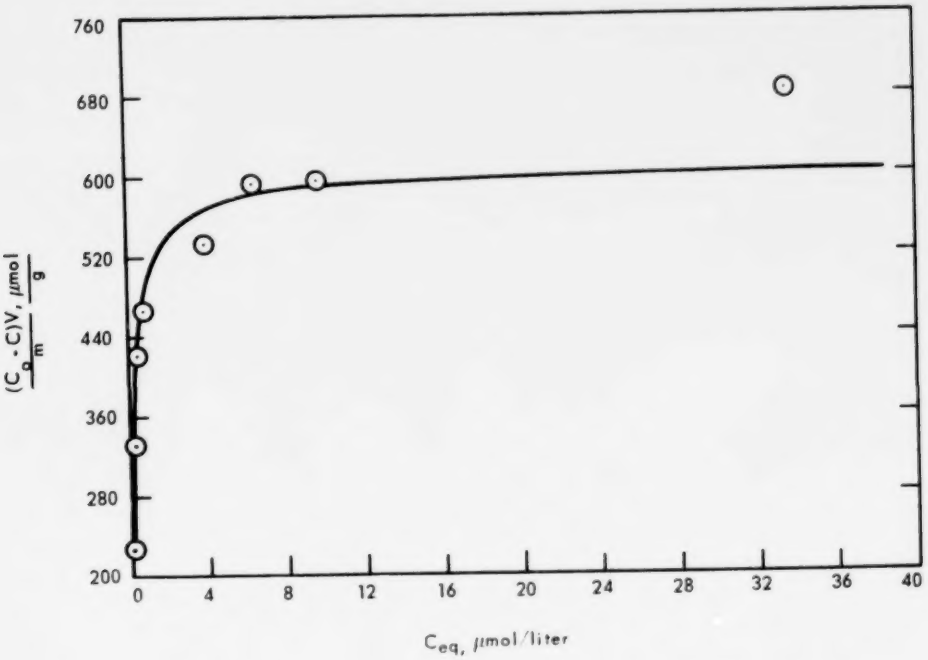
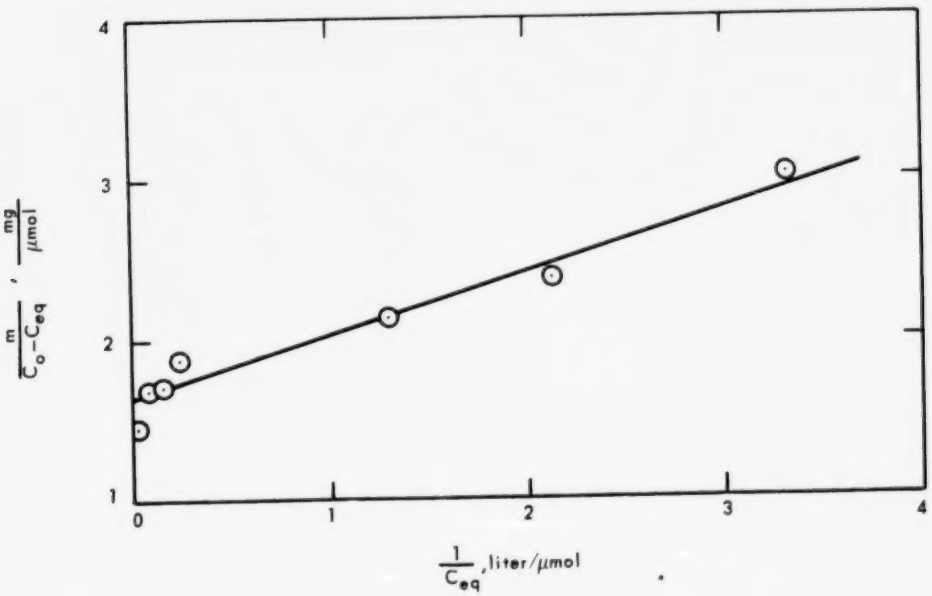


Figure 20. Adsorption isotherm for quinine sulfate.



Attempted correlation of these batch studies with the previous column studies is difficult and probably premature, for neither the batch nor the column studies have been sufficiently complete. The only direct comparison to be made between the batch studies on the rates of adsorption and the continuous-flow studies is with the slopes of the breakthrough curves for the columns. Unfortunately the slopes of the breakthrough curves with the shallow beds used in these studies have not been well enough defined to make such a comparison meaningful. Conversely, the relative amounts of uptake for the individual solutes in the mixture might be compared with data on individual adsorption isotherms in the multicomponent solution, but these latter data have not yet been obtained.

It is tempting to relate the great reduction of rate of uptake of DNOSBP in the multicomponent solution as compared with pure solution with the comparatively low "b" value obtained in the isotherm studies and with the reduced capacity for adsorption shown in the mixed-column studies. Yet, fitting of the Langmuir equation to the equilibrium adsorption data for a substance like DNOSBP that exhibits an apparent X_m value equal to better than 40 percent of the weight of carbon must be admitted to be theoretically meaningless, since the monolayer assumption is certainly invalid.

For the present, then, these results must simply be added to the fundamental data on adsorptive behavior being accumulated for later use when more complete delineation of the systems has been accomplished.

Four Components

Another column study was conducted with a solution containing four different classes of organic compounds, both to determine the adsorptive patterns of some other types of solutes in multicomponent solutions and to investigate breakthrough effects in deeper columns of a carbon more suitable for practical use in waste-water treatment.

A multiple-component solution containing (in mg/liter) Ultrawet K, 24.5; triethanolamine, 15.5; 2,4-dichlorophenol, 16.9; and nonylphenoxypolyethoxyethanol, 53.7, was passed upward through a 1-inch column containing 200 grams of 0.273-millimeter Pittsburgh carbon, at a rate of 2.5 gpm per square foot. The expanded height of the carbon column was 209 centimeters. In addition to routine determinations for concentrations of total organic carbon, ABS, and 2,4-dichlorophenol in the effluent from the column, several 20-liter samples of the effluent were concentrated by vacuum distillation and analyzed by infrared spectrophotometry.

Figure 22 is a plot of data for the uptake of organic material by the Pittsburgh carbon during this 180-hour experiment. The data have been plotted in terms of the organic carbon removed from solution as a function of time. It was possible, as illustrated in Figure 22, to account for the fractions of organic carbon existing as ABS and 2,4-dichloro-

phenol because these materials were determined individually. Although one fraction is represented as being composed of triethanolamine plus nonylphenoxypolyethoxyethanol (9N10), it should be kept in mind that infrared analyses showed complete uptake of 9N10 and considerable leakage of triethanolamine.

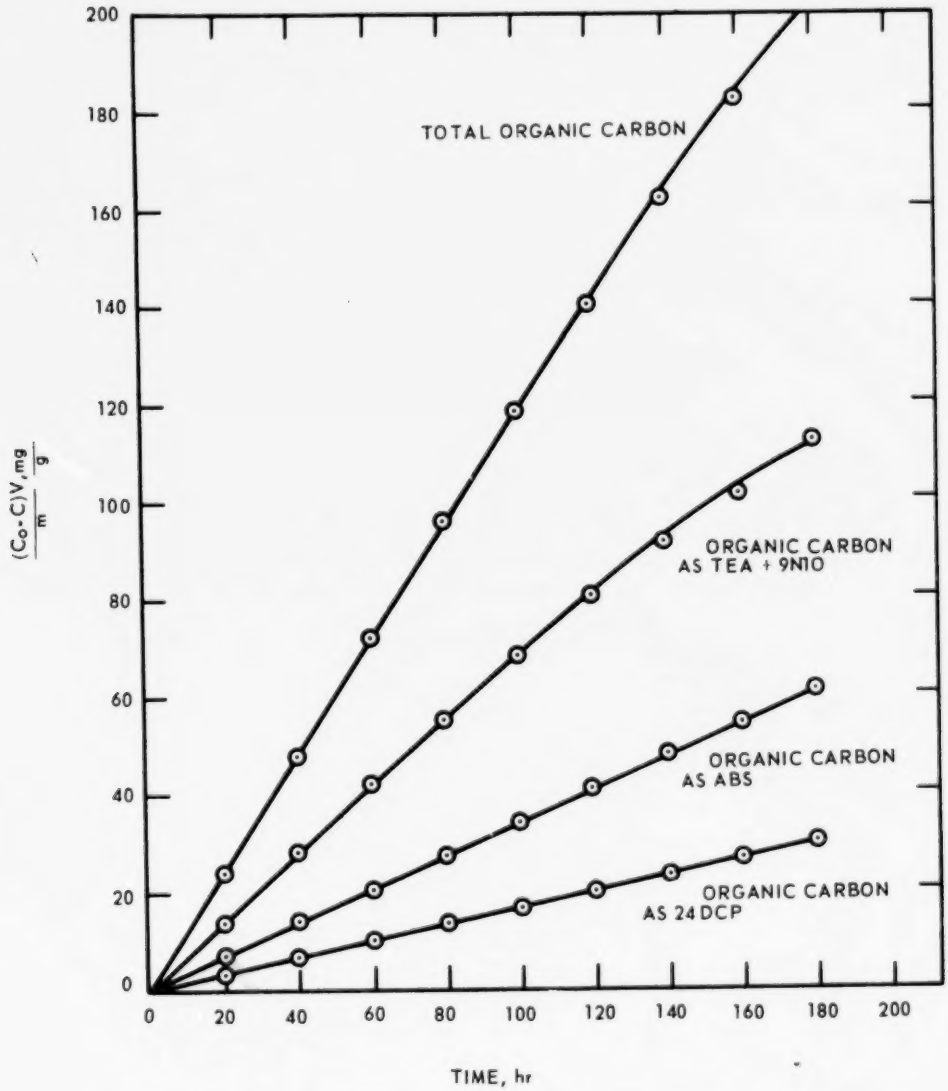


Figure 22. Cumulative adsorption of organic carbon from a mixture of ABS, triethanolamine (tea), nonylphenoxypolyethoxyethanol (9N10), and 2, 4-dichlorophenol (2,4-DCP).

After about 150 hours of operation, maintaining the flow-rate of 2.5 gpm per square foot with the available head of 10 feet became difficult because of increased density of the carbon and clogging of the material in the column. At 180 hours, holding the rate with the experimental apparatus became impossible, and the run was terminated.

After 180 hours the C/C_0 value for total organic carbon in the effluent had reached a value of only about 0.2. No significant concentrations of ABS or 2,4-dichlorophenol were found in the effluent up to this point by standard determinations. The periodic infrared analyses of concentrated effluent indicated that the only material being carried over in the effluent in any significant amount was the triethanolamine; approximately 50 percent of this material was passing completely through the column.

If the weight of the organic carbon in the mixture of organic solutes is taken as one-half the total weight of organic material, then as shown by Figure 22, the total amount of organic material removed from solution by the Pittsburgh carbon during the 180-hour run was about 400 milligrams per gram or a tremendous capacity of 40 percent-by-weight for the carbon to this point. To check this, a mass balance was run by removing the carbon from the column and drying it in a very thin layer at 105°C for 24 hours. The carbon was weighed after drying and found to weigh 279.5 grams! Thus the mass balance confirmed the very high capacity of 40 percent-by-weight. The good capacity realized in this experiment indicates that very high capacities with resulting economy in cost of carbon may be realized for some pollutants.

On the other hand, the early breakthrough of triethanolamine shows that some selectivity in removal of pollutants will be observed in practice and give some indication of the types of compounds that may not be effectively removed by carbon. Batch studies of rate of adsorption and adsorption equilibria should be carried out with triethanolamine.

Eight Components

One column study was run with a very complex mixture of assorted classes of organic solutes. The solutes comprising the mixture, along with their respective concentrations in the influent, are listed in Table 4.

Table 4. COMPOSITION OF EIGHT-COMPONENT SOLUTE MIXTURE

Solute	Concentration in influent, mg/liter
phenol	2.4
quinine	9.3
dodecylsulfate	7.2
sulfonated alkylbenezene	10.6
2-sec-butyl 1-4,6-dinitrophenol	6.0
2,4-dichlorophenoxyacetic acid	5.5
nonylphenoxypolyethoxyethanol	16.5
phenyl N,N'-dimethylphosphorodiamidate	5.0

The column used in this experiment contained 100 grams of 0.273-millimeter Pittsburgh carbon, and the flow rate was 2.5 gpm per square foot. Total organic carbon was the only analytical measure used to determine the effectiveness of the column.

Continuous flow was maintained for approximately 100 hours; then experimental difficulties forced termination of the experiment: for some unexplainable reason prolific microbiological growths developed in the influent solution, presumably made up largely of resistant substrates. At the termination of the run the value of C/C_O for total organic carbon had reached a level of about 0.1, and the total quantity of organic carbon removed from solution up to the time of termination was 8.5 grams. Thus the capacity attained by the adsorbent, up to the point when the experiment was stopped, was on the order of 16 percent on the assumption that the weight of organic matter was twice that of the organic carbon.

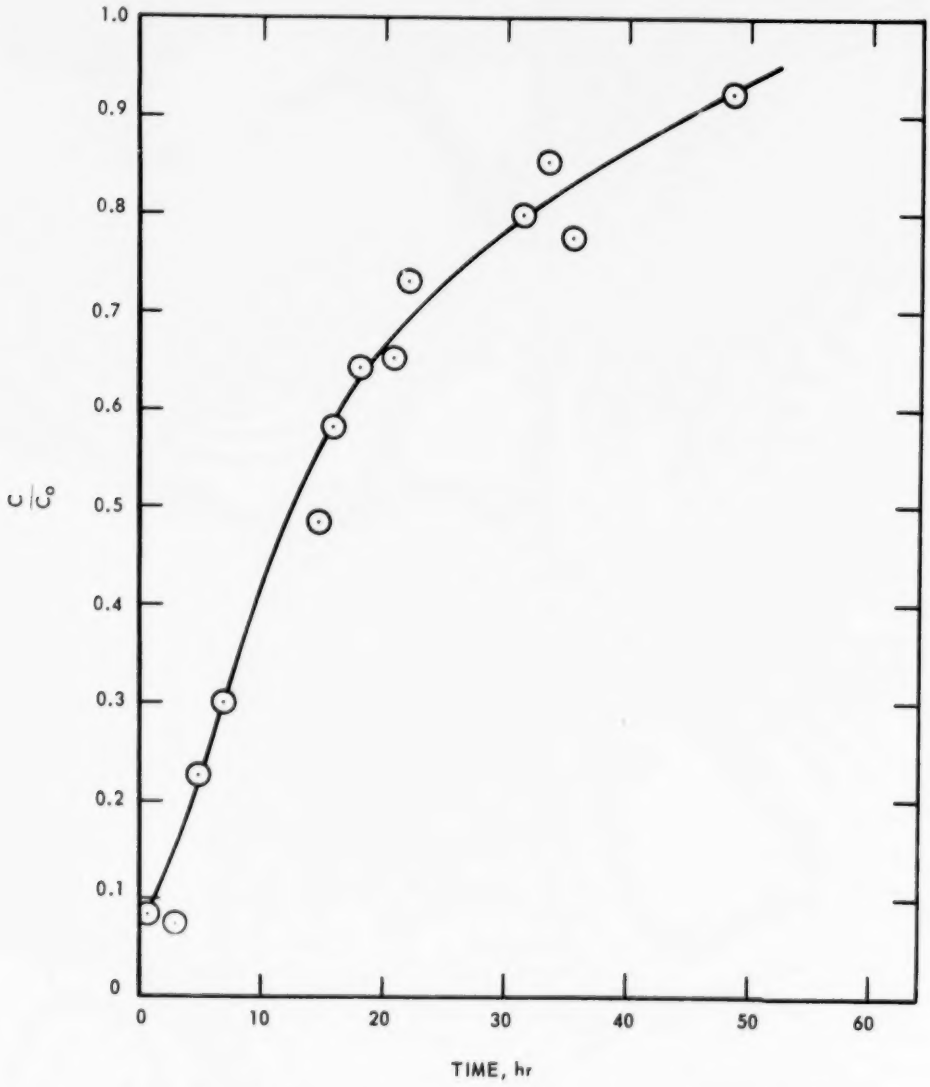


Figure 23. Breakthrough curve for ABS in a column of reused carbon.

SELF REGENERATION OF ACTIVATED CARBON

In a previous study it had been noted that activated carbon tended to regain some of its "initial capacity" upon standing, out of solution. This phenomenon was assumed to occur as a result of continued transport of solute within the pores of the carbon.[24] In further exploration of this phenomenon, carbon from one of the previous column experiments with Ultrawet K (the carbon used in the high-concentration run during the concentration-effect studies) was dried at 105°C for 48 hours and stored for 2 weeks. After drying, the quantity of carbon weighed 52.1 grams, whereas its initial weight before use in the concentration-effect study had been 45 grams. The carbon was then replaced in a column, and a solution containing 77.1 micromoles of Ultrawet K per liter was passed through it at a rate of 2.2 gpm per square foot.

The results of this experiment are shown in Figure 23. While the carbon apparently did regain some of its "initial capacity" in that a typical breakthrough curve starting near $C/C_0 = 0$ was found, the gain in capacity was not great, as indicated by the rapid and complete breakthrough after a relatively short period.

Limited Model for Qualitative Interpretation

Previous research on the kinetics of adsorption on granular carbon from solution in rapidly stirred batch systems has indicated that rates of uptake of organic adsorbates by granular carbon are controlled by intraparticle transport phenomena.[1,25] The curves shown in Figures 4,5, and 6 for the fluidized-column experiments were found, however, not to accord well with curves predicted by mathematical solution of theoretical equations, such as those given by Rosen[26] or Kasten et al.,[27] for processes in columnar or continuous systems controlled by intraparticle diffusion.

Values of the Reynolds numbers for the fluidized systems studied, calculated on the basis of superficial velocities in the columns, were in the range of 0.1 to about 1.0. In this region of apparent laminar flow it is not unreasonable to expect that the over-all rate of transfer of adsorbate from solution phase to the solid adsorbent is controlled by film diffusion processes rather than by intraparticle transport.

Several hypothetical models may be advanced for description of rates for transfer processes, each with its degree of accuracy in representing an experimental system dependent upon the accuracy and the number of limiting assumptions imposed by the model. The most elementary, and therefore most limited, of the several models that may be used to represent the present experimental system will be considered herein; more sophisticated models are presently being developed and will be presented in a subsequent discussion.

The elementary model, which may be more properly termed the "completely mixed-column model," involves assumption of a uniform concentration of adsorbate in the bulk solution over the length of the adsorption column and the assumption that the quantity of adsorbate removed from solution by each particle of carbon in the column is uniform throughout the expanded media. A further limiting assumption imposed by the elementary model is that the equilibrium relationship between adsorbed solute and solute in solution is linear. Obviously, these assumptions are restrictive for application of the elementary model to quantitative description of transfer rates in the experimental system. For example, the experimental isotherms have been determined to follow a Langmuir adsorption pattern, and thus the assumption of linearity involved in the elementary model can provide only an order-of-magnitude approximation for the distribution of adsorbed solute and solute in solution. Further, Figures 2 and 3 show that the distribution of solute in bulk solution is not uniform over the entire length of the adsorption column, and thus the assumption of uniform distribution of solute will result in only an approximation of the actual condition. Observation of considerable particle mixing within the fluidized columns during operation has indicated that the assumption relating to the uniformity of uptake of solute by each particle of adsorbent should not be as restrictive as the two other assumptions.

The authors are fully aware of the limitations of the elementary model and emphasize that this model is not quantitatively representative of the experimental system. The elementary model has, however, a marked advantage of simplicity over more sophisticated models, while still incorporating the major variables of the experimental system. The greatest value of the elementary model, and the reason for its presentation herein, is that it is very useful for delineating qualitatively the effects of the major systemic variables.

Based on the foregoing hypotheses, a relatively straightforward rate equation for transfer of adsorbate from solution to the exterior surface of the adsorbent in a fluidized column may be written. The rate for steady-state transfer of adsorbate across a film to the carbon may be expressed as the ratio of driving force to transfer resistance.

$$\text{Rate of transfer} = \frac{\text{driving force}}{\text{resistance}} = r \qquad (1)$$

The driving force in Equation 1 is the product of the effective concentration difference between the solution and adsorbent and the total area across which transfer occurs. The resistance to transfer is a function of the system and is assumed uniform throughout the system. The transfer resistance is then a coefficient, the reciprocal of which may be termed the transfer coefficient, k.

Equation 1 then takes the form

$$r = k\,a_s M \Delta C \qquad (2)$$

where:

k = transfer coefficient,

a_m = effective transfer area per unit mass of adsorbent,

M_a = mass of adsorbent, and

ΔC = concentration difference across film.

The experimental column operations were carried out under non-steady-state conditions, for which the instantaneous rate of transfer of adsorbate from solution can be expressed in terms of the concentration remaining in solution at any time during the transfer and the concentration gradient across the film at the same instant. Because the adsorbate in the experimental systems had a strong preference for the adsorbent, application of a partition factor, π, to the concentration of adsorbate in the adsorbent is necessary in defining the concentration gradient of the transferable agent across the film. The factor, π, which is equal to the value of C/C_S at equilibrium, serves effectively to increase the concentration-gradient term. Then,

$$Q_m(C_o - C) = k_T\, a_m\, M_a\, (C - \pi C_S) \qquad (3)$$

In Equation 3, Q_m is the mass flow rate of solution (MT^{-1}); C_o is the mass concentration of adsorbate in the influent (MM^{-1}); C is the mass concentration of adsorbate in the effluent at time, t, during the transfer process (MM^{-1}); k_T is the mass transfer coefficient per unit driving force ($MT^{-1}L^{-2}$); and C_S is the mass concentration of adsorbate in the adsorbent at time, t, (MM^{-1}). The value for the instantaneous concentration-gradient term, which incorporates the unknown quantity C_S, is difficult to evaluate experimentally. The value of C_S, however, can be determined by graphical integration of an appropriate expression for the differential quantity of adsorbate transferred to the adsorbent, since the variation of the quantity (C_o-C) with time, t, may be evaluated readily from experimental observations of the variation of C with time.

The differential quantity of adsorbate transferred from solution to the adsorbent may be expressed by the equation

$$\frac{dC_S}{dt} = \frac{Q_m(C_o-C)}{W} \qquad (4)$$

in which W is the total weight of adsorbent (M), and all other terms are as previously defined.

As stated previously, Equation 4 may be integrated graphically to determine a value for C_S, which may in turn be used in Equation 3 to solve for values for the transfer coefficient, k_T. The problem posed

Equation 3 may be circumvented more conveniently in yet another manner. Equation 3 may be differentiated with respect to C to give an expression for dC_s in terms of k_T, dC, and the known quantities Q_m, a_m, π, and M_a. Rearrangement of Equation 3 gives the following expression for πC_s:

$$C_s = C + \frac{Q_m C}{k_T a_m M_a} - \frac{Q_m C_o}{k_T a_m M_a} \tag{5}$$

Equation 5 is then differentiated with respect to C to give

$$dC_s = \frac{1}{\pi} \left(1 + \frac{Q_m}{k_T a_m M_a}\right) dC \tag{6}$$

The right side of Equation 6 is now substituted for dC_s in Equation 4 to give

$$\frac{(1 + Q_m/k_T a_m M_a)\ dC}{dt} = \pi \frac{Q_m (C_o - C)}{W} \tag{7}$$

hence:

$$\int_0^C (k_T a_m M_a + Q_m) \frac{dC}{(C_o - C)} = \int_0^t k_T a_m M_a \pi \frac{Q_m}{W}\ dt \tag{8}$$

Integration of Equation 8 yields

$$\ln \frac{(C_o - C)}{C_o} = - \frac{k_T a_m M_a Q_m \pi}{W (k_T a_m M_a + Q_m)}\ t \tag{9}$$

or

$$C_o - C = C_o e^{-\Sigma t} \tag{10}$$

where

$$\Sigma = \frac{k_T a_m M_a Q_m \pi}{W (k_T a_m M_a + Q_m)}$$

It is apparent from Equation 10 that, if the postulated model is applicable to the description of rates of removal of adsorbate from solution in the experimental fluidized columns, a plot of $\ln (C_o - C)$ versus time should give a straight line with a slope of $-\Sigma$. A somewhat more direct evaluation of values for Σ for various systems can be made by plotting $\ln(1 - C/C_o)$ versus time over a fixed range of the former parameter. Values of Σ may then be calculated by merely dividing the constant difference between $\ln(1 - C_2/C_o)$ and $\ln(1 - C_1/C_o)$ by the increment of time between effluent concentration values of C_1 and C_2. The use of a fixed value for the range of C/C_o further permits a realistic comparison of the performances of different columns. If, for

example, the value of k_T is not constant over an entire run, it would not be valid to compare values of this parameter computed for a fixed time interval for different systems. Such plots have been constructed for the experimental data from the 1-inch column studies, as shown in Figures 24 and 25. In Figure 24 values of $\ln(1-C/C_0)$ versus t are shown for the flow rate studies with 0.273-millimeter Columbia carbon, and in Figure 25 they are shown for the particle size studies with Columbia carbon, and the experiments with Pittsburgh carbon. The value of $C_1/C_0 = 0.1$ has been taken, arbitrarily, as the initiation of significant carryover of adsorbate into the effluent, and $C_2/C_0 = 0.3$, as the point at which the concentration of adsorbate in the effluent has reached an undesirably high level. These plots indicate that the experimental data accord well with the transfer hypothesis over the ranges of C/C_0 used.

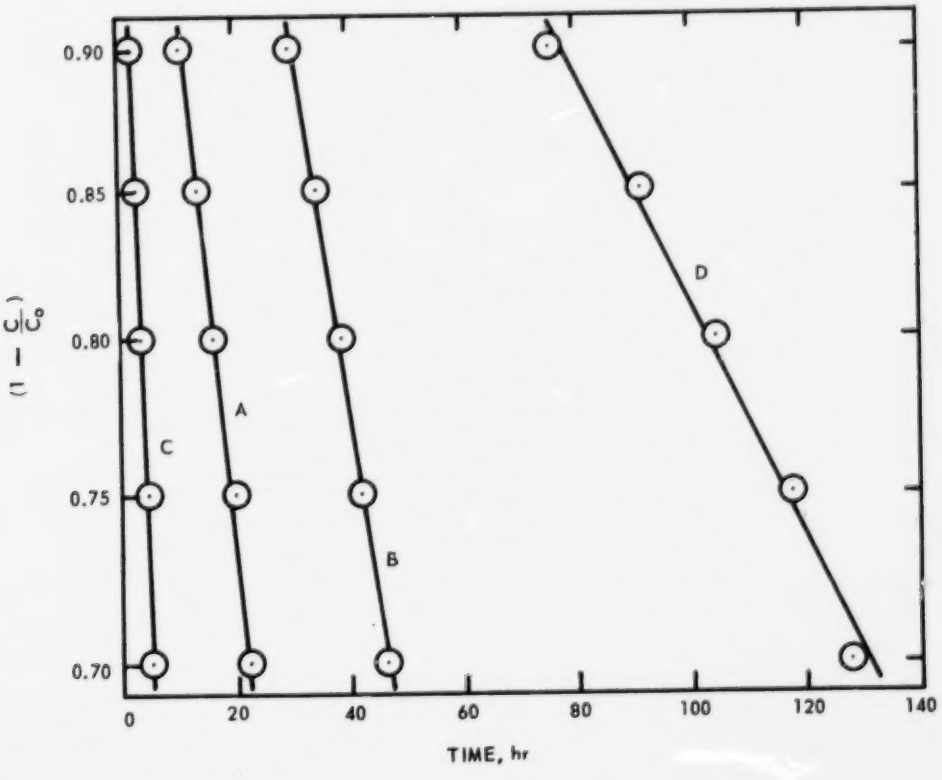


Figure 24. Logarithm of $(1-\frac{C}{C_o})$ as a function of time.

Values for Σ have been calculated from the slopes of the straight lines shown in Figures 24 and 25 and have been tabulated in Table 5 along with those of the parameters needed to compute the corresponding values for k_T, by using the expression

$$k_T = \frac{\Sigma W \quad Q_m}{a_m M_a (Q_m \pi - \Sigma W)} \tag{11}$$

Table 5. TRANSFER COEFFICIENTS AND CORRESPONDING REYNOLDS NUMBERS

Column	$\Sigma \times 10^2$, hr^{-1}	$Q_m \times 10^{-3}$, g/hr	$A \times 10^{-2}$, cm^2	$k_T \times 10^2$, $g/cm^2\text{-}hr\Delta C$	N_R'
A	2.38	3.27	203	19.0	0.55
B	1.56	1.71	203	17.7	0.29
C	8.33	7.29	203	200.4	1.22
D	0.47	0.81	203	3.1	0.14
E	2.00	3.04	299	9.8	0.33
F	3.84	3.00	110	502.4	0.92
G	3.84	3.06	154	272.8	0.68
H	2.08	3.00	240	13.3	0.42
I	2.50	3.07	203	23.2	0.52
K	1.11	3.18	154	35.8	0.70
L	0.89	3.03	375	15.0	0.37

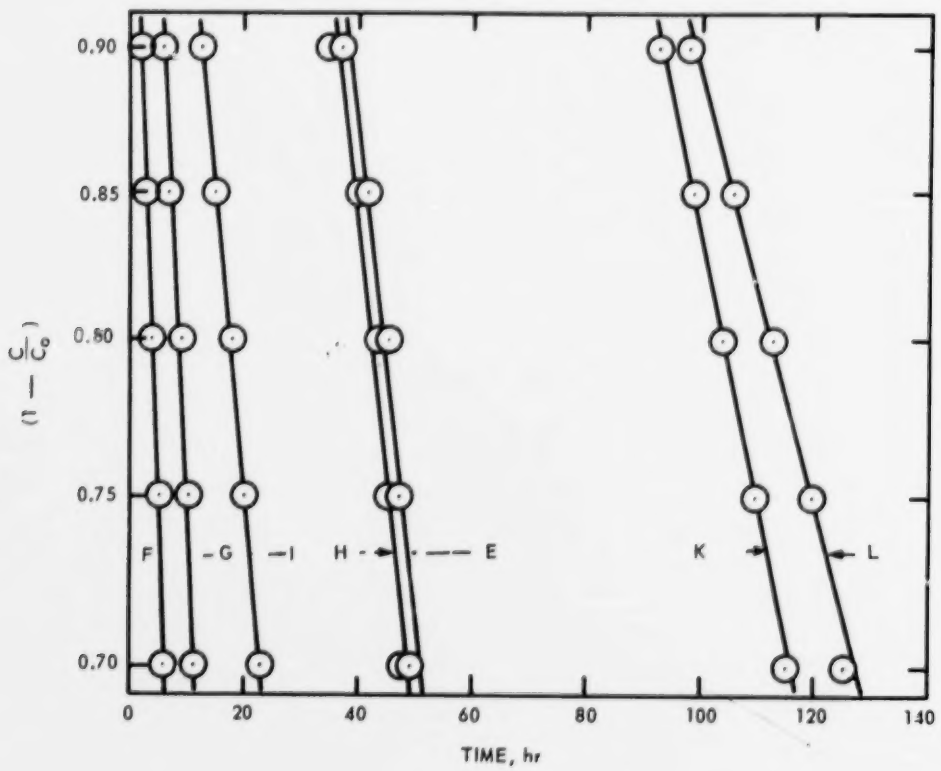


Figure 25. Logarithm of $(1-\frac{C}{C_o})$ as a function of time.

The term A in Table 5 represents the total external surface area across which transfer occurs, and thus is equivalent to the product $a_m M_a$. Values of A have been derived from experimental determinations

of the number of particles per gram for each type of carbon used in the columns, from microscopic observations of shapes and sizes of individual particles,[1] and with knowledge of the mesh sizes of standard sieves through which the particles for each size range have passed and by which they have been retained.

A value of $\pi = 5.6 \times 10^{-4}$ for the Columbia carbon over the concentration range of interest has been taken from the best linear trace of the data for the adsorption isotherm for this carbon; the isotherm for adsorption of the technical ABS on 0.273-millimeter Columbia carbon is shown in Figure 26. The value for π has been taken from a trace from the origin and intersecting a point corresponding to a solution concen-

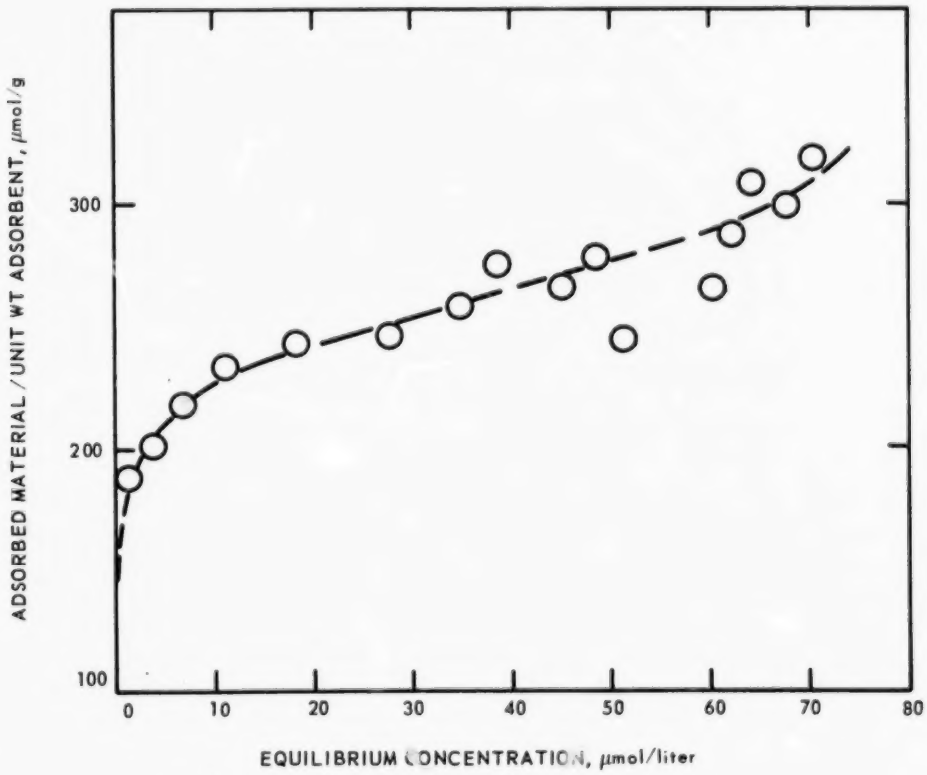


Figure 26. Adsorption isotherm for technical ABS on 0.273-mm Columbia carbon, 30°C.

tration of 70 micromoles per liter and an adsorption level of 310 micromoles per gram. For calculation of π, a value for the density of the carbon of 0.406 gram per cubic centimeter was used. The density of the carbon was determined by weight count and microscopic examination of several hundred particles of the carbon. The value of 0.406 gram per cubic centimeter corresponds to published values for activated carbons.[28]

No steady-state experiments have been carried out during the present investigations for adsorption of the technical ABS on the Pittsburgh carbon. Isothermal equilibrium experiments have, however, been conducted with straight-chain alkylbenzenesulfonates on both Pittsburgh and Columbia carbons. These have demonstrated that the particular grade of Pittsburgh carbon used in the present experiments has a consistently greater capacity for adsorption of the straight-chain compounds than does the grade of Columbia carbon, of comparable size, used in the experiment.

Figure 27 is a plot of typical isotherms for the two carbons; the isotherms shown are for adsorption of 2-decylbenzenesulfonate on 0.273-millimeter carbon. From comparison of these isotherms for the two carbons for comparable systemic conditions and extrapolation of

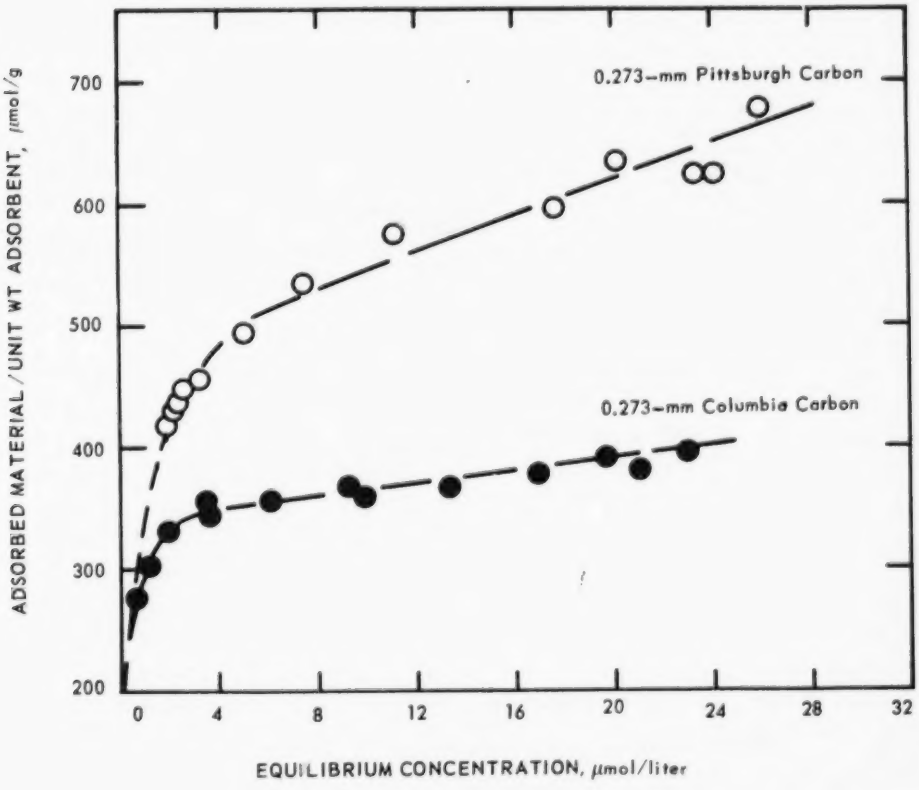


Figure 27. Adsorption isotherms for 2 decylbenzenesulfonate on carbon, 30° C.

the difference to the isotherm for adsorption of the technical ABS on the Columbia carbon, and by use of an experimentally determined value of 0.560 gram per cubic centimeter for the density of the Pittsburgh carbon, a value of $\pi = 2.7 \times 10^{-4}$ was computed for the latter adsorbent in the experimental system.

Particle size and flow rate are both characterized in the dimensionless Reynolds number, N'_R. Thus this group is useful for correlation of the transfer coefficients determined from the experiments with the fluidized columns under different conditions of flow rate and particle size. For calculations of values for a modified Reynolds Number, $N'_R = \frac{vDP}{\mu}$, the velocity term, v, has been taken as the superficial face velocity of flow through the column. The terms D, P, and μ in the Reynolds group are, respectively, the particle diameter, and the density and viscosity of the water.

Values for N'_R are listed in the last column of Table 5; in Figure 28 values of ln k_T are shown plotted against values of ln N'_R. This type of plot is typically used for correlation of heat and mass transfer coefficients with dimensionless groups similar to the modified Reynolds number used in the present correlation.[29] The data are rather well represented by the trace drawn through the points in Figure 28. Thus the postulated model seems adequate over the range taken for description of the rates of adsorption in the experimental fluidized columns.

Implications for Advanced Waste Treatment

Results of laboratory studies indicate that fluidized operation of an activated carbon bed gives qualitatively the same sigmoid relationship for the residual concentration of pollutant that characterizes ordinary packed-bed operation in adsorption or ion exchange. Although many of the experiments do not exhibit the same sharpness of breakthrough associated with columnar operation, it must be kept in mind that these experiments were conducted with very shallow beds of adsorbent and for the most part with relatively high flow rates. The developing sharpness with decreasing flow rate and with decreasing particle size implies that with deeper columns (several feet of adsorbent) and with flow rates of a few gallons per minute per square foot, sigmoid curves in which a large fraction of the ultimate capacity will be used before appreciable breakthrough occurs should be realized.

That such breakthrough patterns are observed in spite of the apparent complete mixing of adsorbent particles in the column seems to be related to the fact that adsorption of material by the carbon results in an increased density for the carbon. As adsorption proceeds, the rate of flow of liquid up through the carbon bed must be continuously increased to maintain the same degree of expansion.

As adsorption proceeds, the nearly saturated particles are lifted less than fresh ones. Consequently, there is stratification in the bed, with nearly exhausted adsorbent at the bottom at the point of inflow and

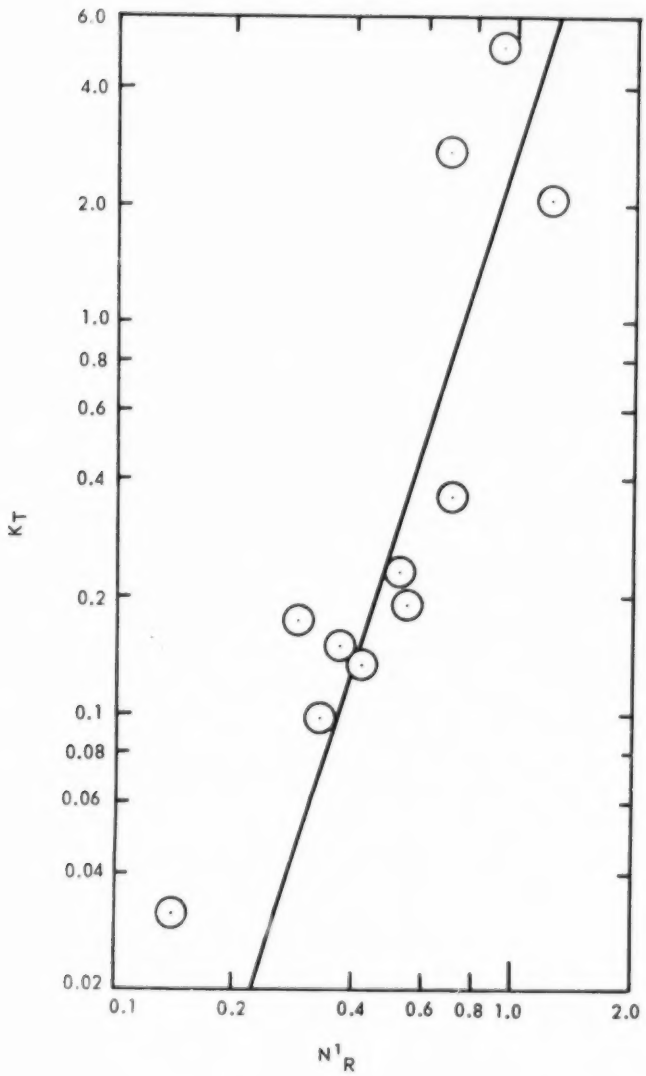


Figure 28. Correlation of transfer coefficient with Reynolds number.

with fresh particles at the top to provide a polishing effect. Thus true counter-current operation is approximately maintained despite the considerable continuous agitation of the bed.

Such segregation is advantageous also because continuous withdrawal of material from the bottom of the bed will remove only substantially saturated carbon, thus essentially full utilization of capacity can be obtained before regeneration.

Summarization of data for an appropriate set of comparable column experiments in a form that perhaps more clearly justifies these conclusions is shown in Table 6. For compilation of this table from data for the initial column experiments, A to I, the point at which the concentration of organic matter in the effluent was equal to 0.3 of that in the influent was taken as representing practical exhaustion of the column. This arbitrary figure was convenient to use, and the conclusions would not have been changed qualitatively had another fraction been selected.

Table 6. CAPACITIES OF FLUIDIZED CARBON COLUMNS TO 0.3 BREAKTHROUGH

Column	Flow rate, liters/hr	Volume of effluent at $C/C_0 = 0.3$, liters	Adsorption to $C/C_0 = 0.3$, μmol/g/liter	Adsorption to $C/C_0 = 0.3$, μmol/g	% of total input of adsorbate adsorbed to $C/C_0 = 0.3$
A	3.27	68.7	1.4	96.2	94
B	1.71	77.0	1.4	107.8	97
C	7.29	43.7	1.3	56.8	86
D	0.81	102.1	1.5	153.2	97
E	3.04	149.0	1.6	238.4	95
F	2.99	20.9	1.3	27.2	75
G	3.06	39.8	1.6	63.7	92
H	3.00	138.0	1.5	207.0	90
I	3.07	67.5	1.5	101.3	94

Column three of Table 6 shows the volume of liquid passed through each bed up to the selected breakthrough point. These volumes vary with the rate of flow and particle size of the carbon. The fourth column is simply the influent concentration less the mean effluent concentration divided by the weight of carbon in each column. When the figures in columns 3 and 4 are multiplied, the amount of adsorption that has occurred up to the selected breakthrough period is obtained. The ultimate capacity of the carbon is about 300 micromoles per gram. Most of the experiments, therefore, showed about a third to a half of ultimate capacity at the time of breakthrough with just 8 to 9 inches of settled bed. The fine-particle carbon (run E), however, showed almost 80 per-

cent realization of capacity at this point, while the coarse-particle material (run F) had reached only 10 percent of capacity. Variations with flow rate are less dramatic, but there is a marked increase with decreasing flow rate as shown by runs A, B, C, and D, in which the other variables all have the same value.

Nonetheless, all of the beds except runs C and F show better than 90 percent total removal of organic matter over the period up to the selected breakthrough point. If multiple columns in parallel are used - some fresh and some nearly at the breakthrough point - or if an effluent holding reservoir is provided, use of 0.3 as the breakthrough point is not unreasonable from a practical standpoint.

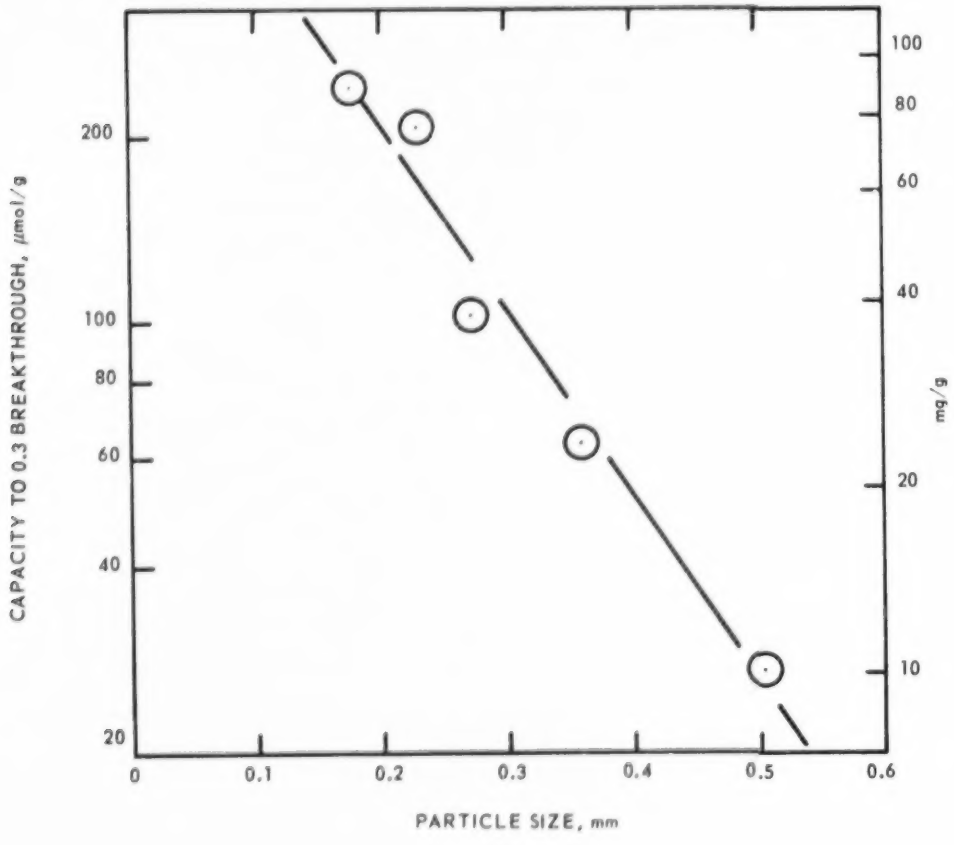


Figure 29. Total solute adsorbed per unit weight of adsorbent to 0.3 breakthrough as a function of particle size, 45 g Columbia carbon, flow rate = 2.5 gpm/ft ^{2}.

Figure 29 shows more quantitatively the variation of capacity to this 0.3 breakthrough point. The plot would indicate that full capacity should be realized at a rate of 2.5 gallons per minute per square foot in a 9-inch bed with particle diameters less than about 0.13 millimeter.

Undoubtedly the relationship actually tapers off as adsorption near capacity is reached; however, additional relationships of this sort obtained with deeper beds should be significant and interesting.

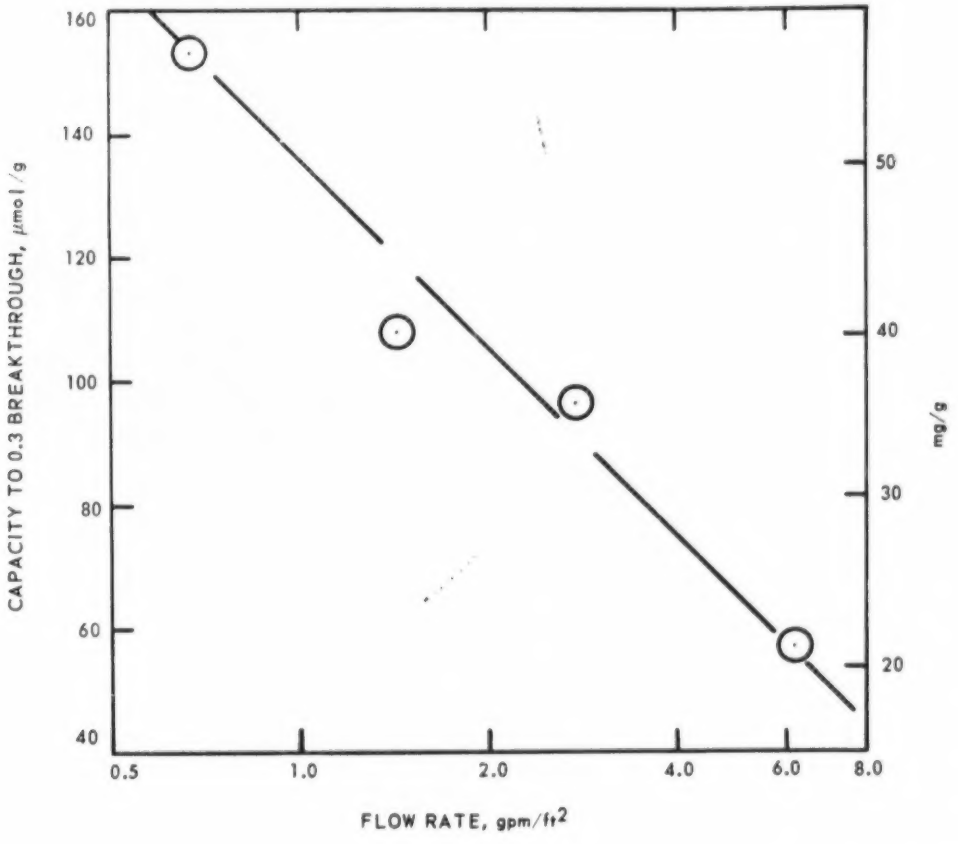


Figure 30. Total solute adsorbed per unit weight of adsorbent to 0.3 breakthrough as a function of flow rate, 45 g 0.273-mm Columbia carbon.

Similarly Figure 30 shows the quantitative relationship between flow rate and realized capacity. Here the need for data with deeper beds is even more pronounced to reach a higher percentage of ultimate capacity at the time of breakthrough.

Figure 31 illustrates the difference between the breakthrough curve and the total uptake indicated by the figures in the last column of Table 7. The illustration is for run D, the one with the low flow rate. The ratio of the area under the locus of the experimental points to that under the straight line is the percent uptake of the organic material.

Finally, Figure 32 shows plots of runs A, B, C, D, with scales of reduced variables that seem useful in correlating data from these and subsequent runs. It should also serve as a good representation for initial determination of the practicability of a given method of operation.

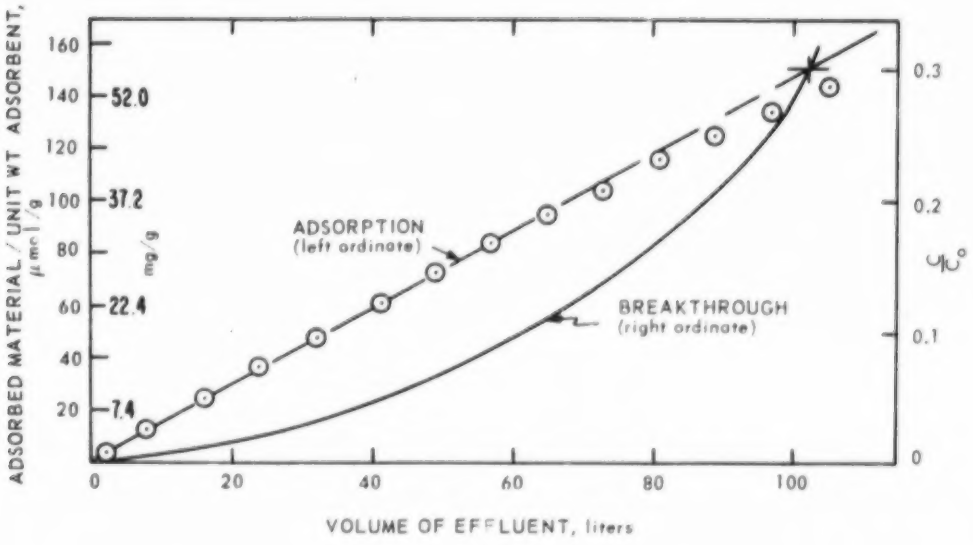


Figure 31. Adsorption and breakthrough for column D as functions of volume of effluent, 45 g 0.273-mm Columbia carbon, flow rate = 0.68 gpm/ft^2.

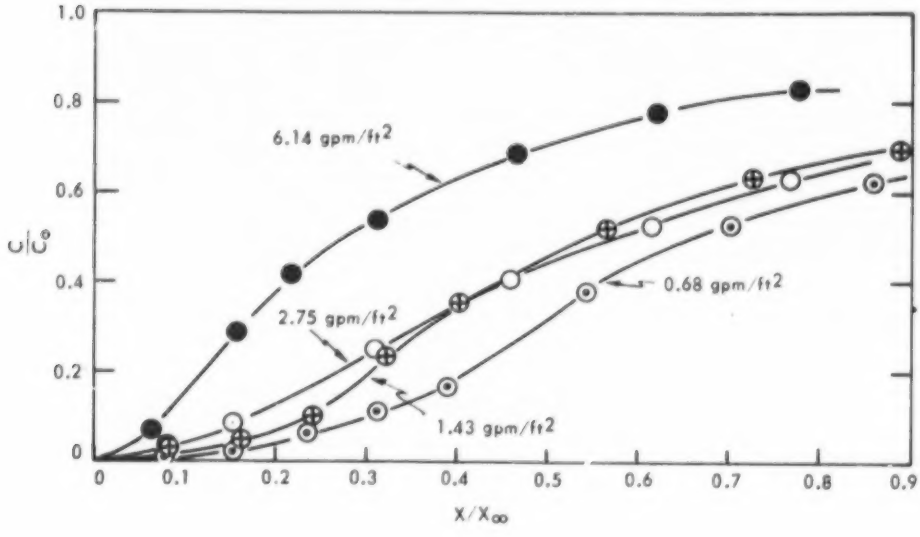


Figure 32. Ratio of effluent concentration to influent concentration as a function of ratio of quantity adsorbed per gram to capacity after infinite time for different flow rates, 45 g 0.273-mm Columbia carbon.

ADSORPTION ON CARBON IN BATCH-TYPE SYSTEMS

Extensive investigations of kinetics and equilibria of adsorption in batch-type systems have been described in an earlier report.[1] To supplement some of the information provided by the earlier investigations, additional experiments have been conducted with batch systems. These experiments have included studies of adsorption kinetics and adsorption equilibria with simple systems composed of different types of carbon and different compounds than those previously reported, and some studies with complex mixtures of organic compounds.

The inferences that may be drawn from the present investigations accord with those set out in the earlier report: thus the data are presented mainly for comparison of additional systems with those previously described.

The Columbia LC carbon used in the earlier studies of adsorption in batch systems was chosen for study because it satisfied operational requirements, and not because it is the most desirable material for practical application to waste-water treatment. Indeed, the Columbia carbon is relatively expensive in comparison with other commercially available carbons and does not provide as high values for rates and capacities of adsorption as some others do. Testing the performance of other commercially available carbons was, therefore, desirable. The materials chosen for study were Pittsburgh carbon (Pittsburgh Chemical Co.), Darco carbon (Atlas Powder Co.), and Norit carbon (American Norit Co.). Some rates of adsorption with the Darco and Norit carbons relative to that of the Columbia carbon have been reported previously;[1] the additional rate studies have been limited to the Pittsburgh carbon. All four carbons have been comparatively tested in studies of adsorption equilibria.

Rates of Adsorption

ADSORPTION ON PITTSBURGH CARBON

Rates of uptake of technical grade ABS were studied for various particle sizes of Pittsburgh carbon. Results of these experiments are shown in Figure 33.

The relative rate constants for these systems taken from the slopes of the straight lines in Figure 33 range from 20 micromoles per gram/(hour)$^{1/2}$ [7.4 mg/g (hr)$^{1/2}$] for 1.545-millimeter carbon to 105 micromoles per gram/(hour)$^{1/2}$ [39.1 mg/g (hr)$^{1/2}$] for 0.200-millimeter

carbon. Previous studies have indicated that the value of the relative rate constant for adsorption of the technical ABS by 0.126-millimeter Columbia carbon is 52 micromoles per gram/(hour)$^{1/2}$ [19.4 mg/g (hr)$^{1/2}$].[1] The relative rate constant predicted for 0.200-millimeter Columbia carbon, from the dependence of this parameter on the inverse square of particle diameter,[1] is about four-tenths of 52, or approximately 21 micromoles per gram/(hour)$^{1/2}$. Thus the Pittsburgh carbon has been found to exhibit a rate constant for adsorption about five times as large as that for Columbia carbon in systems with technical ABS. The notably greater rate for the Pittsburgh carbon in the rapidly stirred batch system, in which intraparticle transport is quite probably rate controlling, can presumably be attributed to larger pore diameters, which permit more rapid transport of the highly branched technical ABS. This effect should decrease with decreasing molecular size and complexity of the adsorbate.

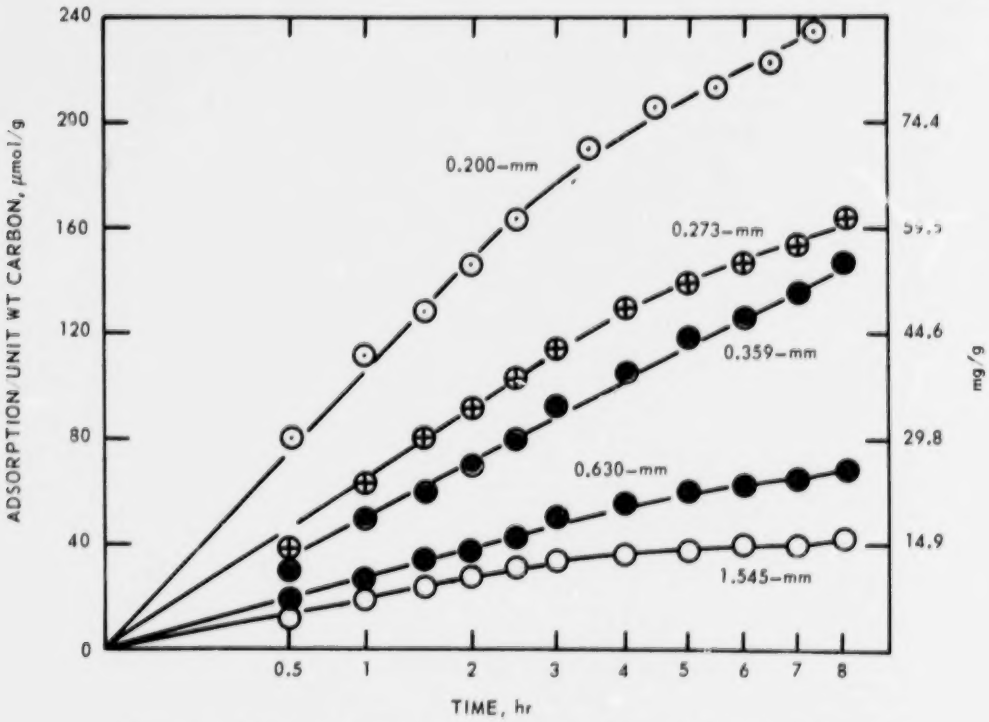


Figure 33. Rates of adsorption of technical ABS on Pittsburgh carbons of different particle size, 100 mg/liter carbon, 30° C.

The relative rate constants for the different sizes of Pittsburgh carbon correlate well with the square of the inverse of particle diameter, as illustrated in Figure 34. This correlation accords with that noted for different sizes of Columbia carbon,[1] and identical conclusions may be drawn.

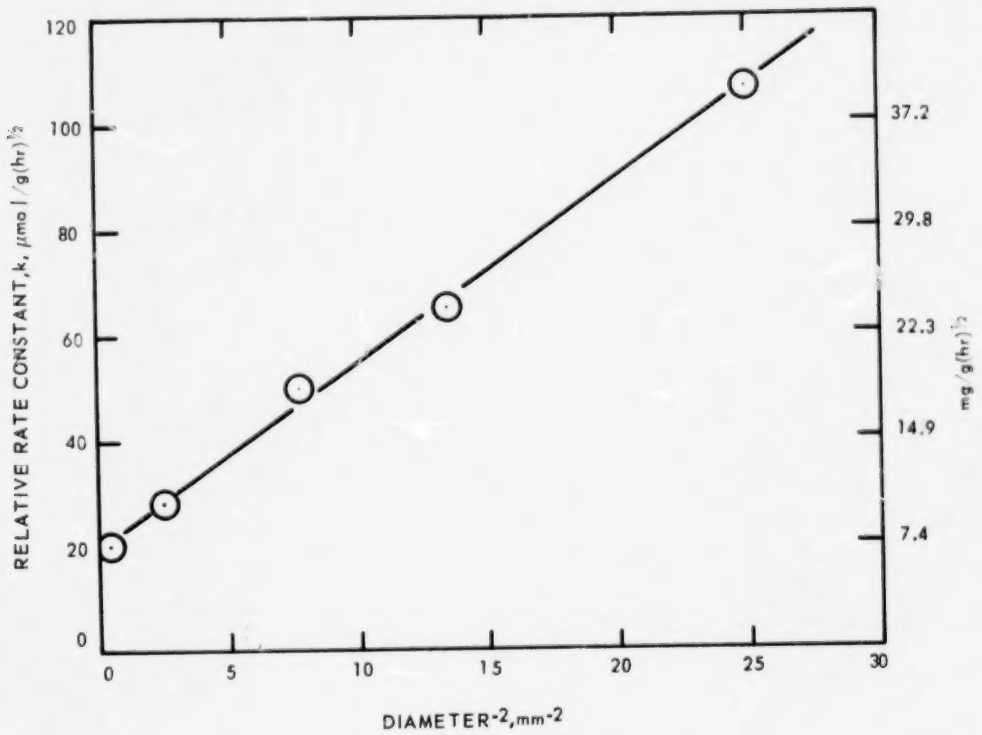


Figure 34. Relative rate constant as a function of the inverse of the square of particle diameter; 100mg/liter Pittsburgh carbon technical ABS 30° C.

ADSORPTION FROM MIXTURES OF ORGANIC COMPOUNDS

An investigation of the rate of adsorption on carbon from a complex mixture of organic compounds typical of the resistant materials that might be expected to occur in some combination in waste effluents was carried out to gain some insight into the characteristics of adsorption from complex mixtures. The results of the rate experiment with a mixture of technical ABS, nonylphenoxylnonylethoxyethanol, dichlorodiphenyltrichloroethane, nicotinic acid, and triethanolamine are illustrated in Figure 35.

The relative rate constant for the data shown in Figure 35 is 15 milligrams per gram/(hour)$^{1/2}$ or 1 5 percent by-weight adsorption per (hour)$^{1/2}$ for the 0.273-millimeter Columbia carbon. For adsorption of the technical ABS alone on 0.126-millimeter Columbia carbon, the relative rate constant has a value of about 52 micromoles per gram/(hour)$^{1/2}$ or 19.4 milligrams per gram/(hour)$^{1/2}$.[1] Extrapolation of this relative rate constant to 0.273-millimeter carbon gives a value of approximately 4 milligrams of total material per gram/(hour)$^{1/2}$ as against nearly four times this much for adsorption of organic carbon alone from the mixture. The increased total rate thus noted is in accord with previous observations for studies of competitive adsorption in bisolute systems.[28] The much larger initial concentration in the

mixed solutions (C_O = 29.5 mg organic carbon/liter) must contribute in part to the increased rate of adsorption.

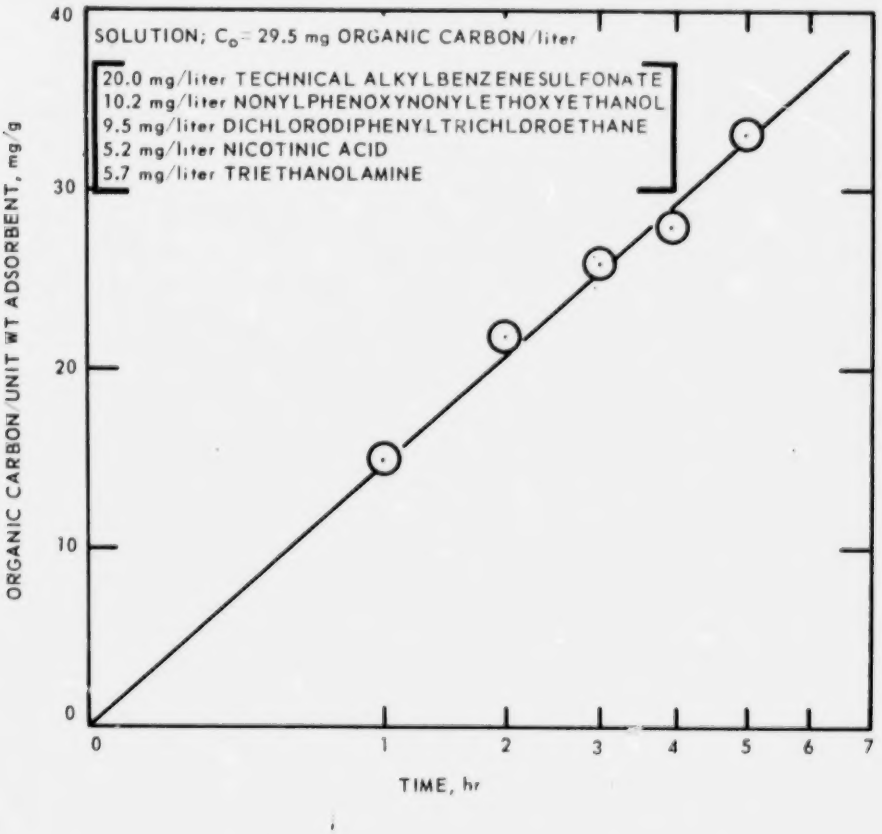


Figure 35. Rate of adsorption organic carbon from a mixture of organic compounds by carbon; 500 mg/liter 0.273-mm Columbia carbon, 30 C.

Equilibria and Capacities for Adsorption

EFFECT OF PARTICLE SIZE

The increase of capacity of carbon with decreasing particle size noted tentatively in the first report [1] has been investigated in more detail. Data from isotherms for the adsorption of 3-dodecylbenzenesulfonate on three different sizes of Columbia carbon at 30°C are shown in Figure 36. An increase in capacity with decreasing particle size is apparent and appears significant. The quantity of solute adsorbed per unit weight of carbon for equilibrium concentrations in solution corresponding to apparent monolayer saturation of the carbon has been found to correlate with the inverse of the diameter squared for the data

plotted in Figure 36. This correlation is illustrated in Figure 37. Thus an increase in capacity of approximately 50 percent results in reduction of diameter by a factor of two.

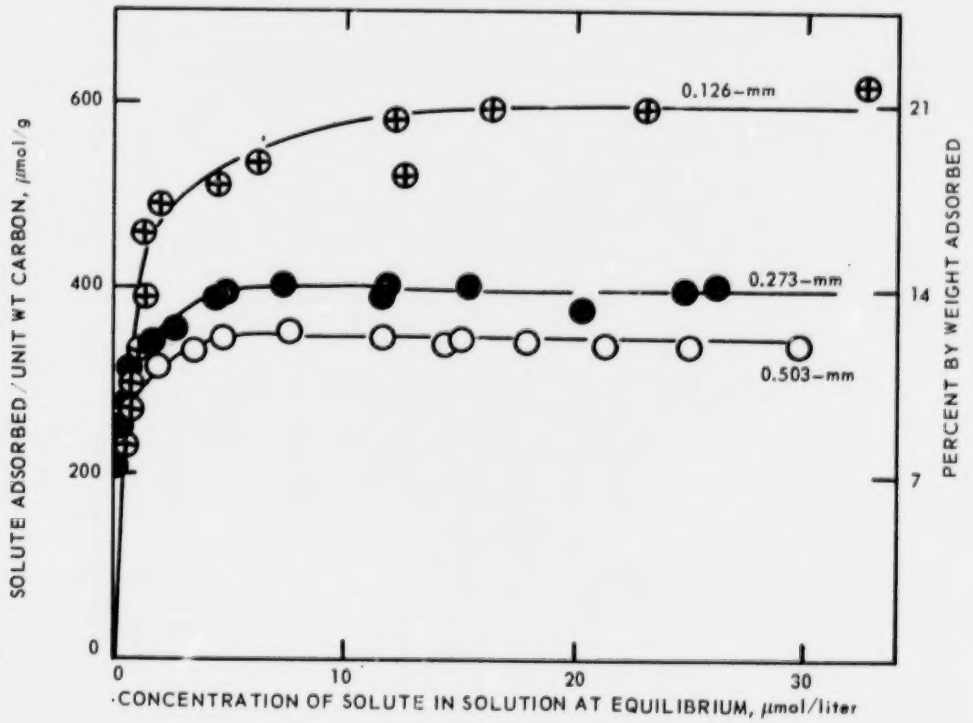


Figure 36. Isotherms for adsorption of 3-dodecylbenzenesulfonate by carbons of different particle size; Columbia carbon, 30° C.

ISOTHERMS FOR DIFFERENT CARBONS

In Figure 38, data obtained in studies on equilibria of adsorption of 2-decylbenzenesulfonate on different commercially available 0.273-millimeter carbons have been plotted. The Pittsburgh carbon apparently has a much greater capacity for this surfactant than does any of the other carbons tested, more than 20 percent by weight for solution concentrations of 20 micromoles per liter (6.5 mg/liter) or greater. Moreover, the capacity of the Pittsburgh carbon equilibrium increases more with increase in solute concentration than does that for any of the other adsorbents studied.

Because of its relatively large capacity and high rate of uptake, the Pittsburgh carbon appears more suitable than the other studied for application to waste-water treatment.

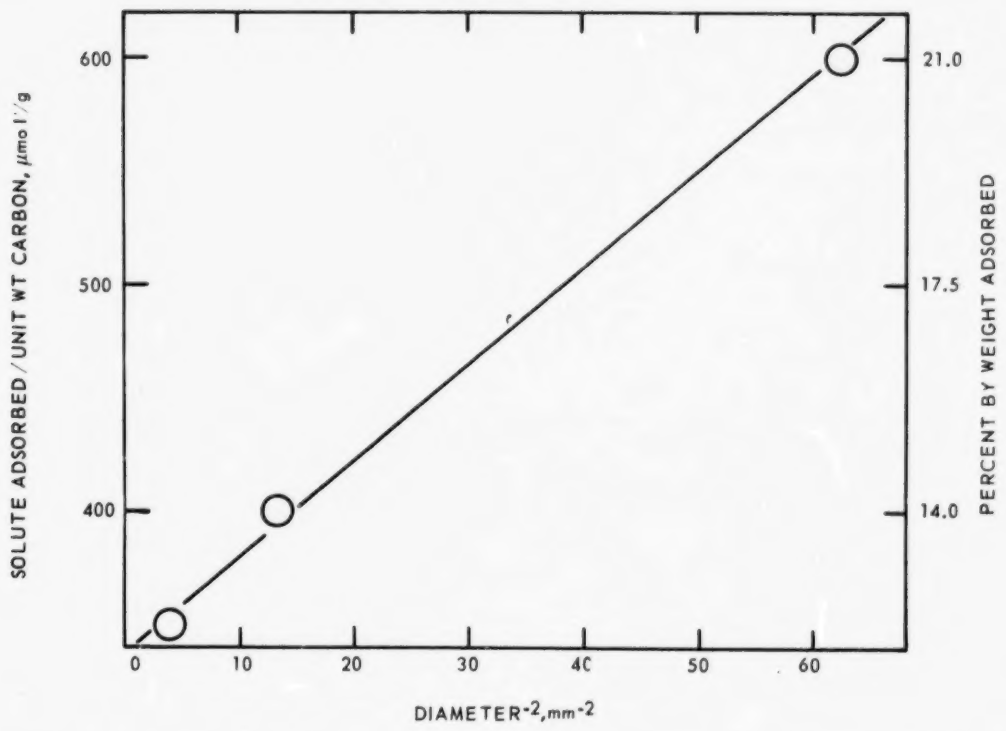


Figure 37. Plateau value for adsorption isotherm as a function of the inverse of the square of particle diameter; 3-dodecylbenzenesulfonate, Columbia carbon, 30° C.

ISOTHERMS FOR ADSORPTION OF NITROCHLOROBENZENES ON CARBON

The occurrence of nitrochlorobenzenes as discharged waste in river waters has been noted by Middleton.[30] Previous studies on rates of adsorption of this compound by carbon have been reported.[1] To supplement the previous information on the characteristics of adsorption of this pollutant, investigations of adsorption equilibria have been carried out.

The Columbia carbon used in the present experiments appears to have a remarkably large capacity (nearly 40% by weight) for adsorption of nitrochlorobenzene, as may be observed from the data shown in Figure 39. This large capacity may be due in part to the fact that the nitrochlorobenzenes are only slightly soluble in water (the solute was originally dispersed in the water by dilution of a 10^{-2} M solution of nitrochlorobenzene in methanol). Thus the equilibrium is strongly in favor of deposition of material in the pore spaces of the carbon.

ISOTHERM FOR A MIXTURE OF ORGANIC COMPOUNDS

The equilibria of adsorption from a complex mixture of organic compounds, identical to the mixture used in the rate studies described previously, were investigated by using 0.273-millimeter Columbia

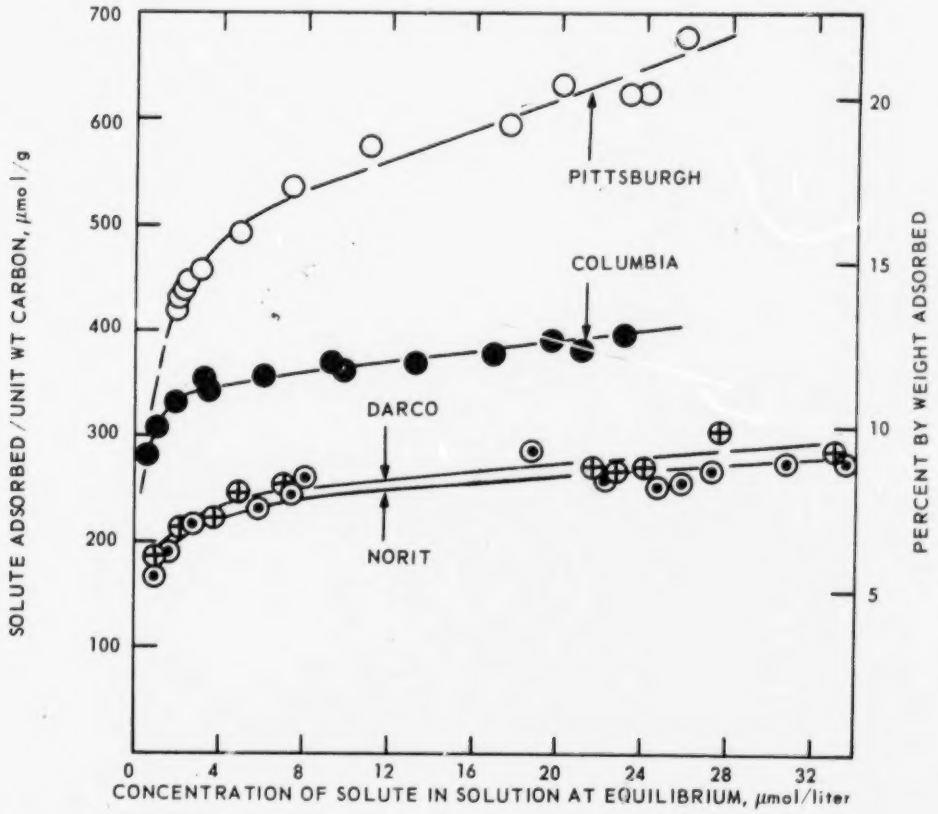


Figure 38. Isotherms for adsorption of 2-decylbenzenesulfonate on different carbons; 0.273-mm particle size, 30° C.

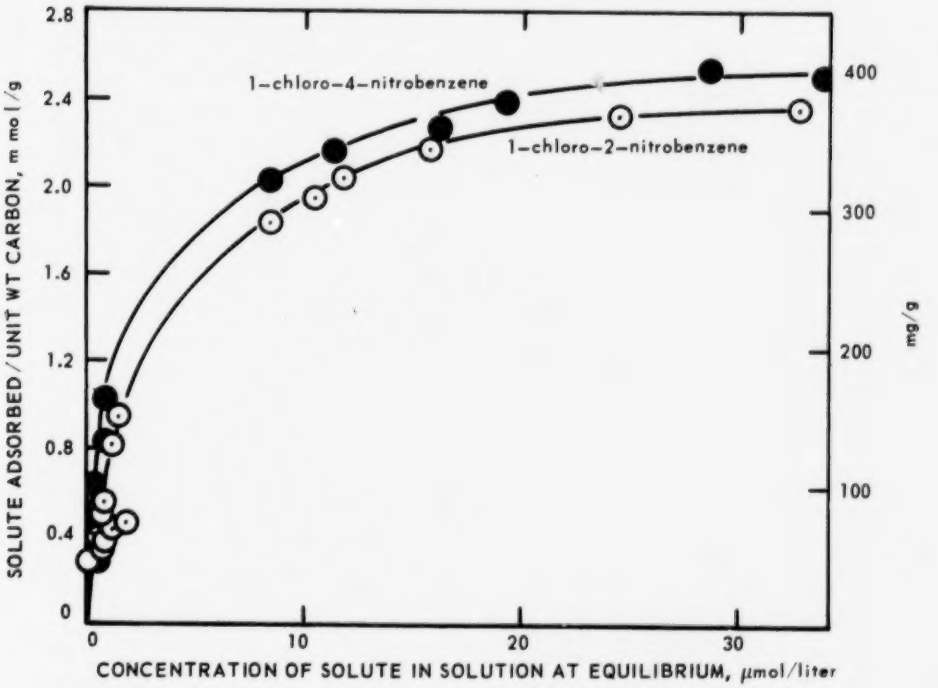


Figure 39. Isotherms for adsorption of nitrochlorobenzenes on carbon; 0.503-mm Columbia carbon, 30° C.

carbon. The isotherm obtained from these studies is shown in Figure 40. Organic carbon was used as a measure of the extent of adsorption.

Obviously, from Figure 40, the capacity of the carbon is enhanced considerably in the presence of several compounds as compared with that obtained in single-solute solutions.[1]

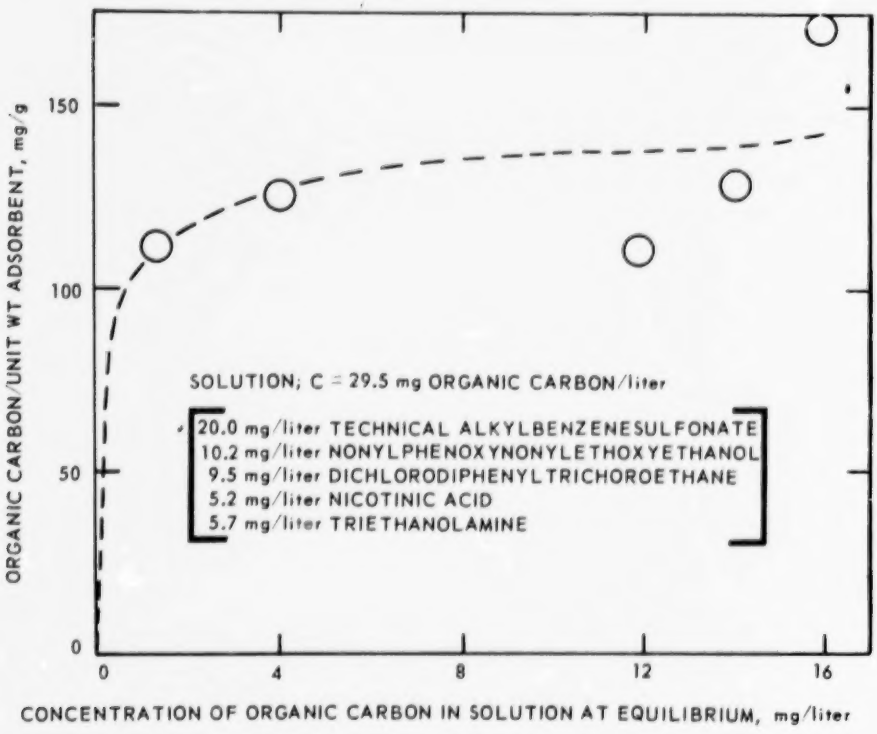


Figure 40. Isotherm for adsorption of organic carbon from a mixture of organic compounds by carbon; 0.273-mm Columbia carbon, 30° C.

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ADSORPTION OF ORGANIC PESTICIDES ON CARBON

Environmental dispersal of organic pesticides has been a matter of much recent and widespread concern. The increased use of organic pesticides in agricultural, domestic, and industrial applications and the consequent increase in the occurrence of these materials in water and wastes have brought about a potential hazard for the health and well-being of the public.[31]

Adsorption by carbon appears to have promise as a technique for removing potentially harmful pesticides from waters and wastes. Accordingly, studies of rates and equilibria of adsorption have been extended to a number of representative pesticides or substances molecularly related to them.

Pesticide materials chosen for study include compounds of different chemical classes, typical of various types of herbicides, acaricides, and insecticides. The pesticides studied, along with some of their significant properties, are listed in Table 7.

As shown in Table 7, the chemical classes represented by the pesticides studied include thiophosphates (0,0-diethyl-0-p-nitrophenyl phosphorothioate), carbamates (1-naphtyl N-methylcarbamate), dinitrophenols (2-sec-butyl-4, 6-dinitrophenol and 2-cyclohexyl-4,6-dinitrophenol), and chlorophenoxy acids [2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, and 2-(2,4,5-trichlorophenoxy) propionic acid].

The 0,0-diethyl-0-p-nitrophenyl phosphorothioate (Parathion) was obtained from the American Cyanamid Company; the 1-naphthyl-N-methylcarbamate (Sevin), from the R.A. Taft Sanitary Engineering Center (U.S. Public Health Service); and the remainder of the compounds, from the Dow Chemical Company. All compounds as obtained were described by the suppliers as being chemically "pure" relative to the active chemical agent.

Columbia LC coconut carbon was used as the adsorbent in all experiments with the pesticides. Prior to use in the experiments, the adsorbent was separated by thorough sieving into uniform particle sizes, after which portions of suitable size range were washed in distilled water to remove any leachable impurities and adherent powder, and dried at 105°C. The size range chosen for the present studies included those particles passing a U.S. Standard Sieve No. 50 and being retained on a No. 60 sieve; the mean particle diameter for this size range is 0.273 millimeter.

Table 7. SELECTED ORGANIC PESTICIDES

Compound	Primary application	Molecular weight	Approximate solubility in water at 25°C, mg/liter
2,4-dichlorophenoxyacetic acid	herbicide	221.0	900
2,4,5-trichlorophenoxyacetic acid	herbicide	255.5	280
2-(2,4,5-trichlorophenoxy)-propionic acid	herbicide	269.5	180
2-sec-butyl-4,6-dinitro-phenol	herbicide, insecticide	240.2	52
2-cyclohexyl-4,6-dinitro-phenol	acaricide, insecticide	266.2	10
1-naphthyl N-methylcarbamate	insecticide	201.2	99
0,0-diethyl-0-p-nitrophenyl phosphorothioate	acaricide, insecticide	291.3	24

To eliminate from the experimental systems all extraneous material that might have introduced sources of error and interference, all solutions of the pesticides used in the experimental systems were prepared with twice-distilled water. Cambridge tap water was first distilled in a conventional tin-lined still, and the condensate was transferred into an all-glass still for redistillation. Preliminary boiling with escape of steam was used to purge the water of dissolved carbon dioxide and chlorine before collection of the condensate from the redistillation.

Experimental Details

ANALYTICAL METHODS

Of the substances investigated, only Parathion does not exhibit a characteristic absorption spectrum suitable for direct measurement of concentration within the ranges used in the present experiments. Spectra for the six other pesticides are shown in Figures 41 through 46.

The analytical method employed for Parathion takes advantage of the ease with which the phosphorus-oxygen bond in that material is cleaved by hydroxide. The hydrolysis produces a mole of p-nitrophenol

for each mole of Parathion originally present in solution. Because p-nitrophenol has a well-defined absorption spectrum with a high molar absorptivity at the wavelength of maximum adsorption (400 mμ), and because the reaction to form p-nitrophenol from Parathion is rapid and quantitative, the method provides a reliable and sensitive means for analysis of Parathion.

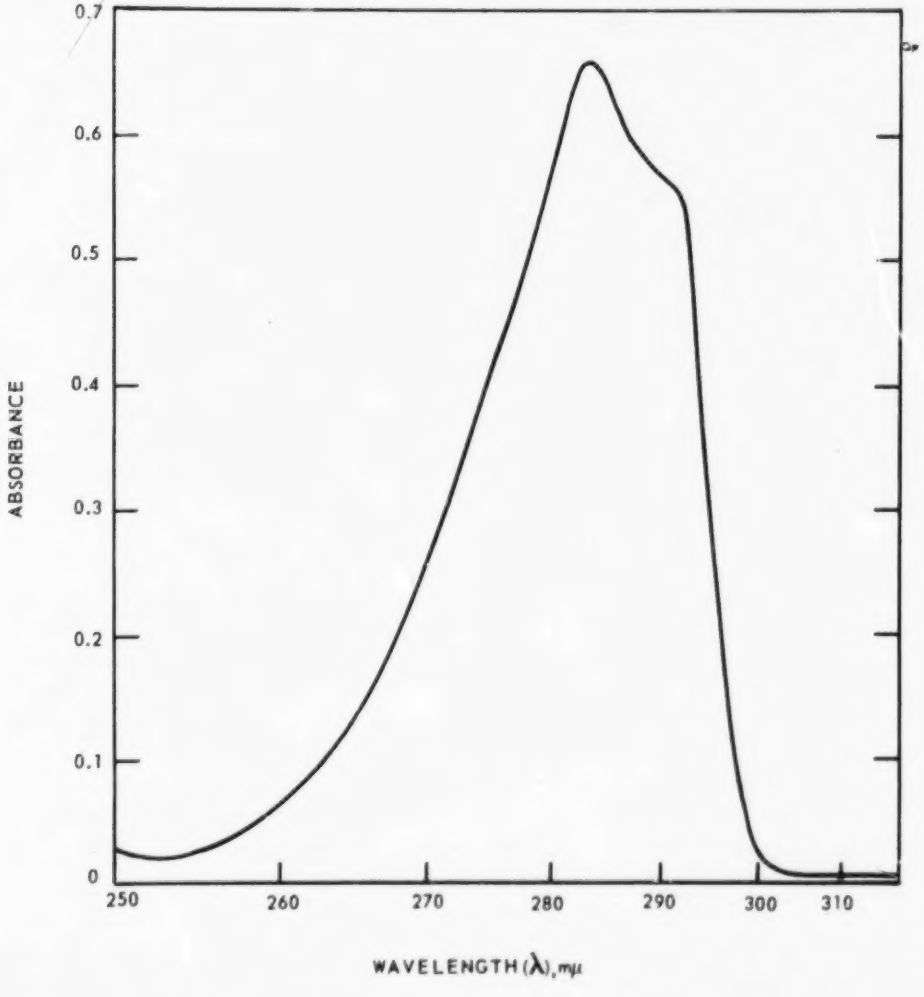

Figure 41. Absorption spectrum for 2,4-dichlorophenoxy-acetic acid; cell length 5 cm, C = 70 μmol/liter.

For fairly concentrated samples (1-100 μ M), about 10 milliliters of 1 N KOH were added to 50 milliliters of sample. The mixture was heated to boiling, allowed to cool, diluted to 100 milliliters, and then the absorbance at 400 millimicrons was measured in a cell of appropriate length. For more dilute samples, 3 KOH pellets were added to a 100-milliliter sample, and the procedure outlined above was repeated. The lower limit of the method is about 50 nanomoles per liter with a 10-centimeter cell. The absorption spectrum for p-nitrophenol is shown in Figure 47.

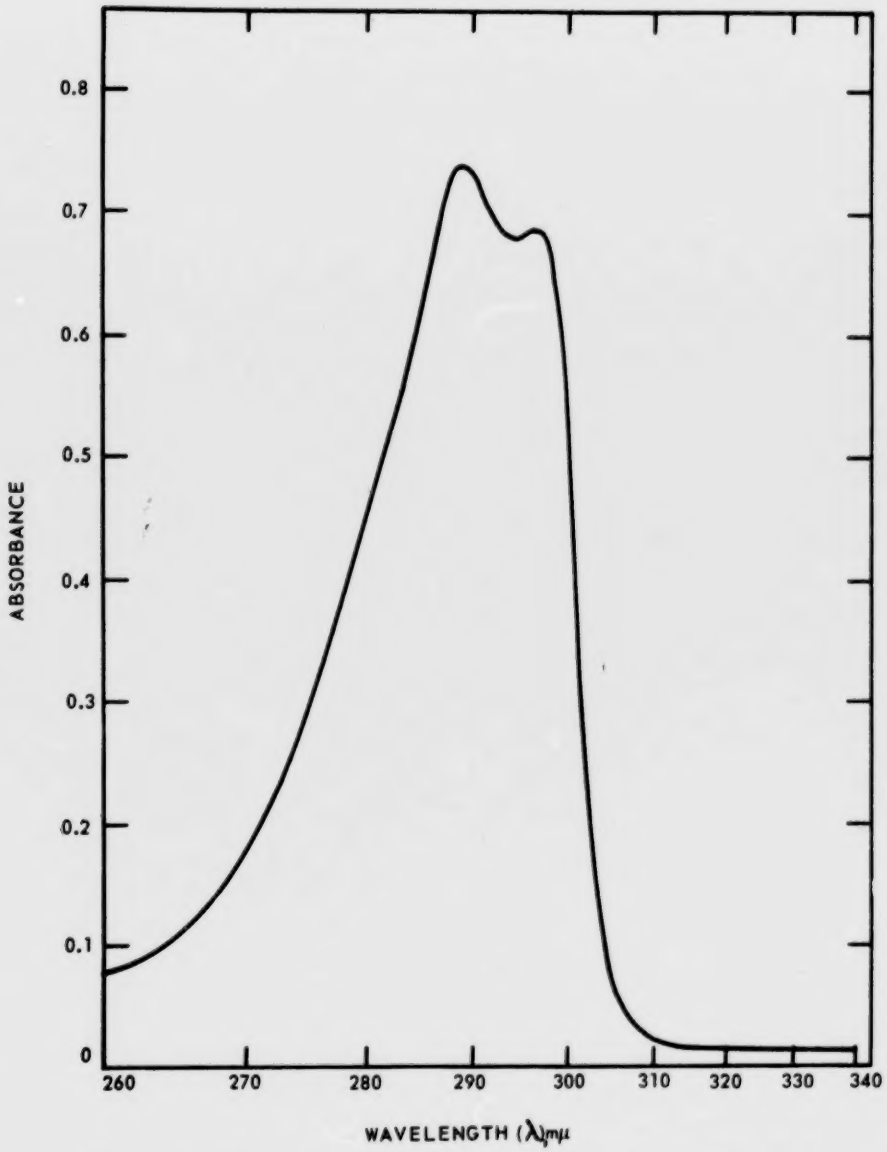

Figure 42. Absorption spectrum for 2,4,5-trichlorophenoxyacetic acid; cell length 5 cm, C = 60 μmol/liter.

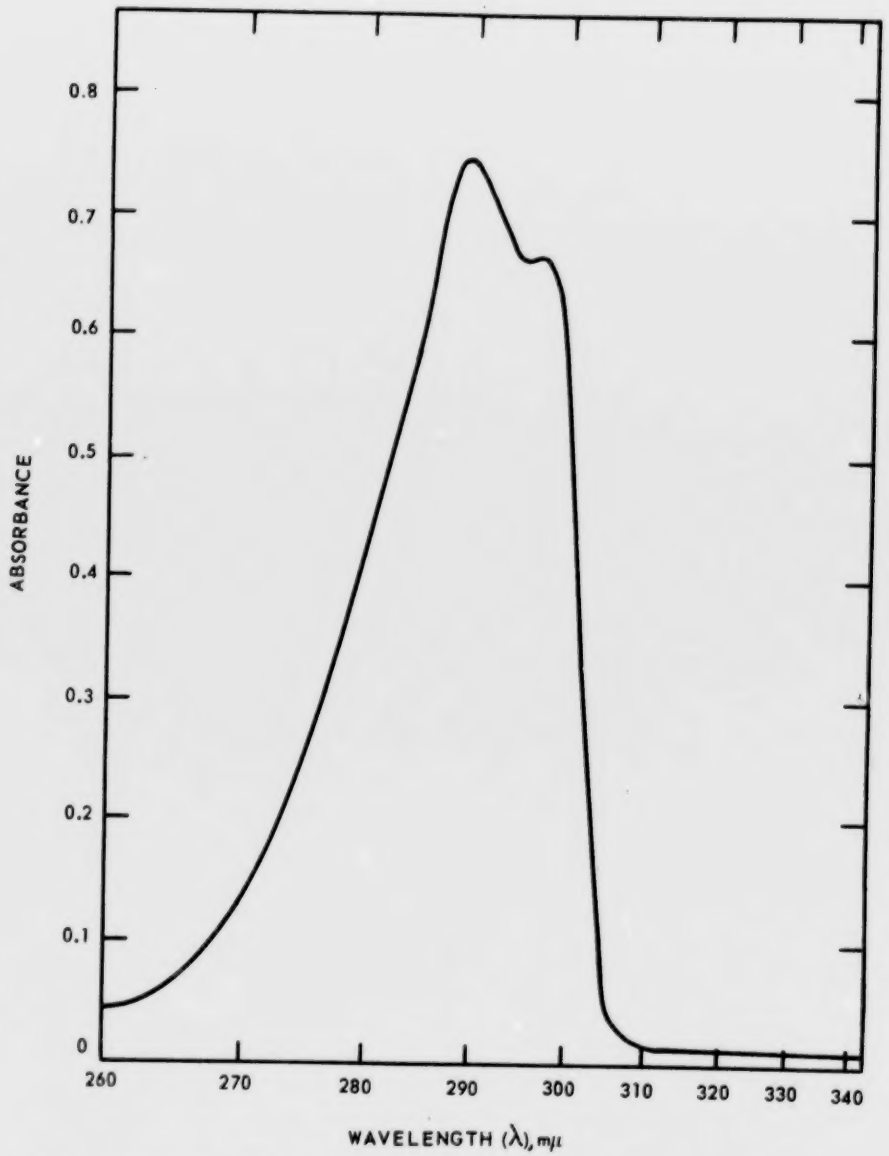

Figure 43. Absorption spectrum for 2-(2,4,5-trichlorophenoxy)-propionic acid; cell length 5 cm, C = 60 μmol/liter.

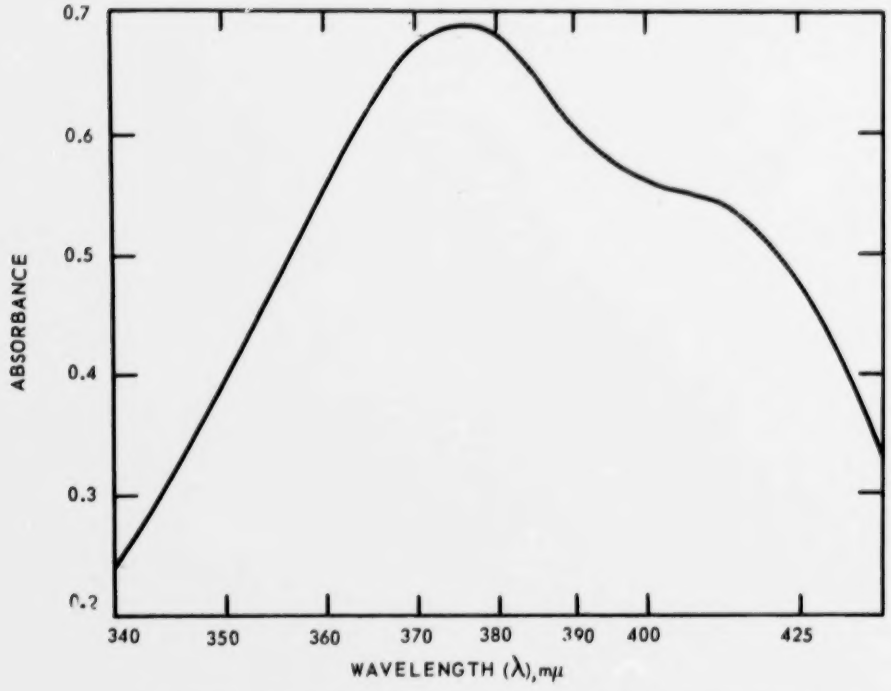

Figure 44. Absorption spectrum for 2-sec-butyl-4,6-dinitrophenol; cell length 1 cm, C = 50 μmol/liter.

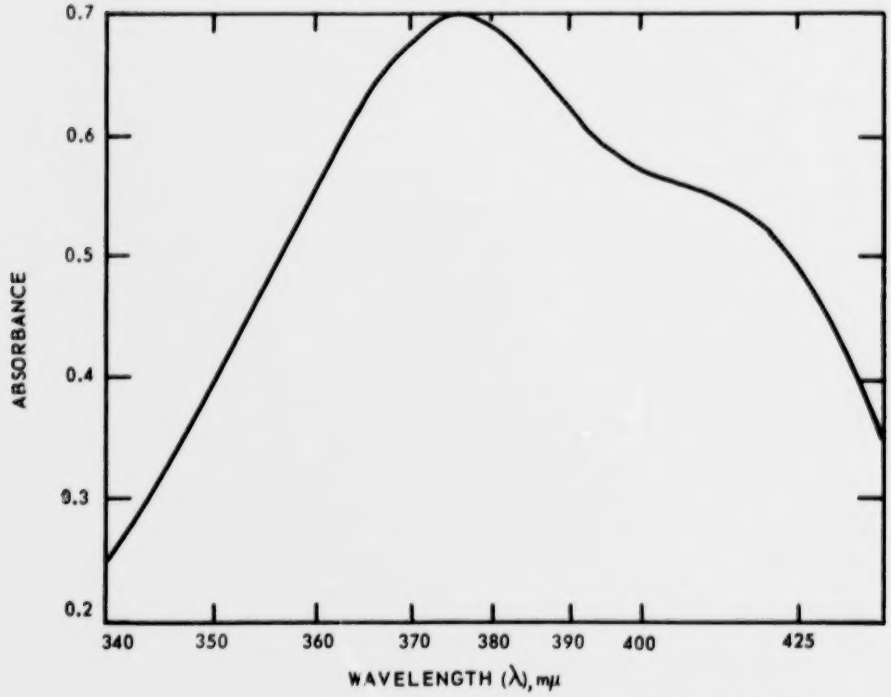

Figure 45. Absorption spectrum for 2-cyclohexyl-4,6-dinitrophenol; cell length 1 cm, C = 50 μmol/liter.

After measurement of the absorption spectrum for each solute had been made with a Beckman Model DK-2 spectrophotometer, the absorption maximum for solutions of each of the substances was located precisely with a Beckman Model DU spectrophotometer by measuring intensities of absorption for a localized region on both sides of the wavelength of maximum absorption indicated by the spectra obtained with the Model DK-2. Subsequent spectrophotometric measurements were made with the Model DU.

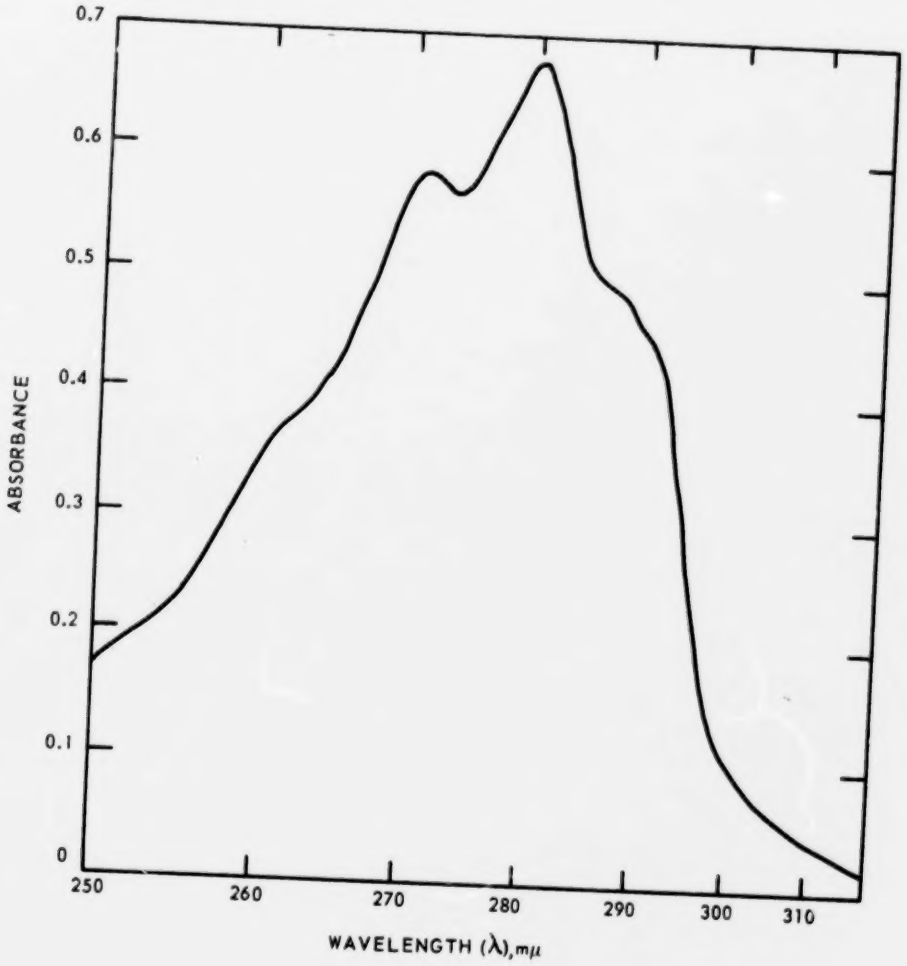

Figure 46. Absorption spectrum for 2-naphthyl-n-methylcarbamate; cell length 5 cm, C = 23 μmol/liter.

Calibration curves for all the solutes are given in Figures 48 through 54. Wavelengths of maximum absorption, and observed values for the molar absorptivity for each material are listed in Table 8.

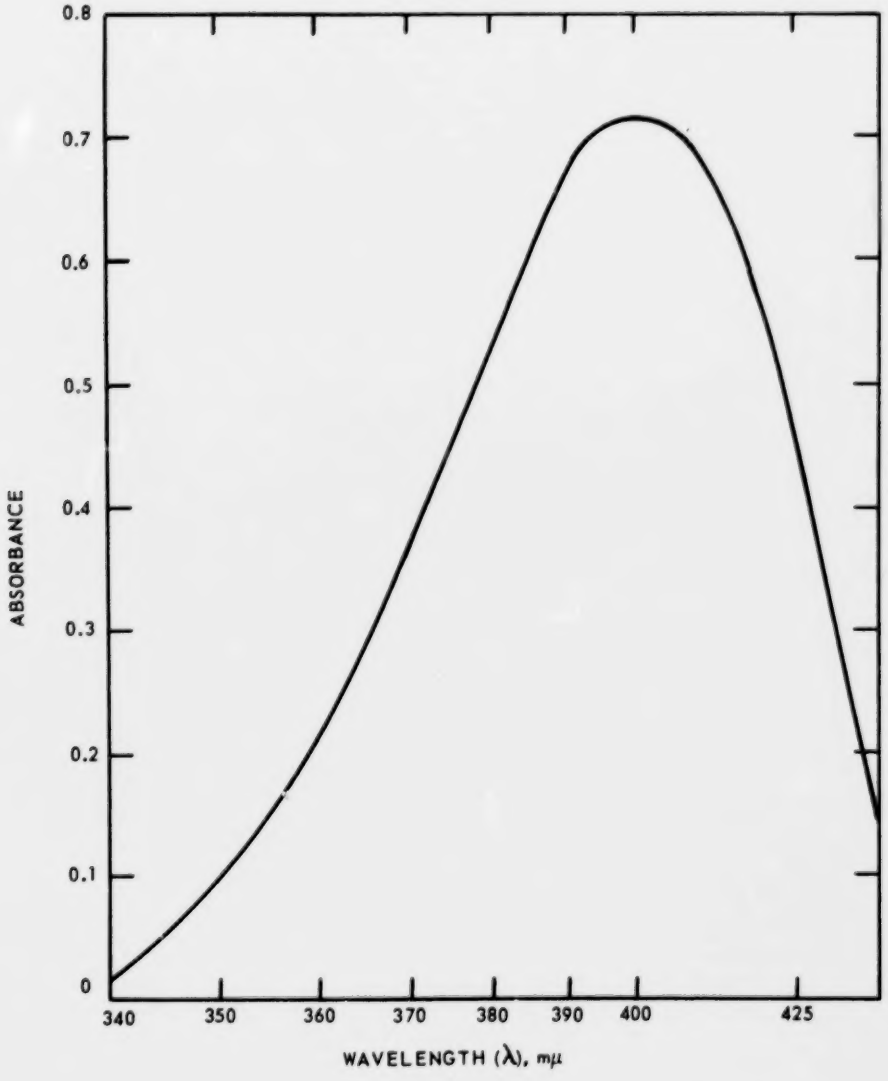

Figure 47. Adsorption spectrum for p-nitrophenol, cell length 1 cm, C = 40 μmol/liter.

Table 8. ANALYTICAL DATA FOR ORGANIC PESTICIDES

Compound	Wavelength of maximum absorption, mμ	Molar absorptivity, (cm^2/mol) x 10^{-6}
2,4-dichlorophenoxy-acetic acid	284	1.9
2,4,5-trichlorophenoxy-acetic acid	289	2.5
2-(2,4,5-trichloro-phenoxy) propionic acid	289	2.5
2-sec-butyl-4,6-dinitrophenol	375	14.5
2-cyclohyxyl-4,6-dinitrophenol	376	14.0
1-naphthyl-N-methylcarbamate	279	5.9
p-nitrophenol (for Parathion)	400	18.0

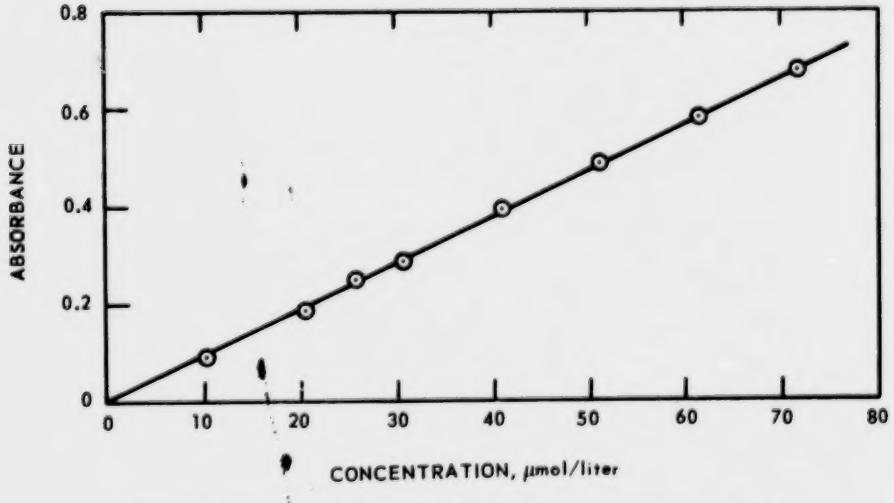

Figure 48. Calibration curve for 2,4-dichlorophenoxyacetic acid; cell length 5 cm, λ = 284 mμ.

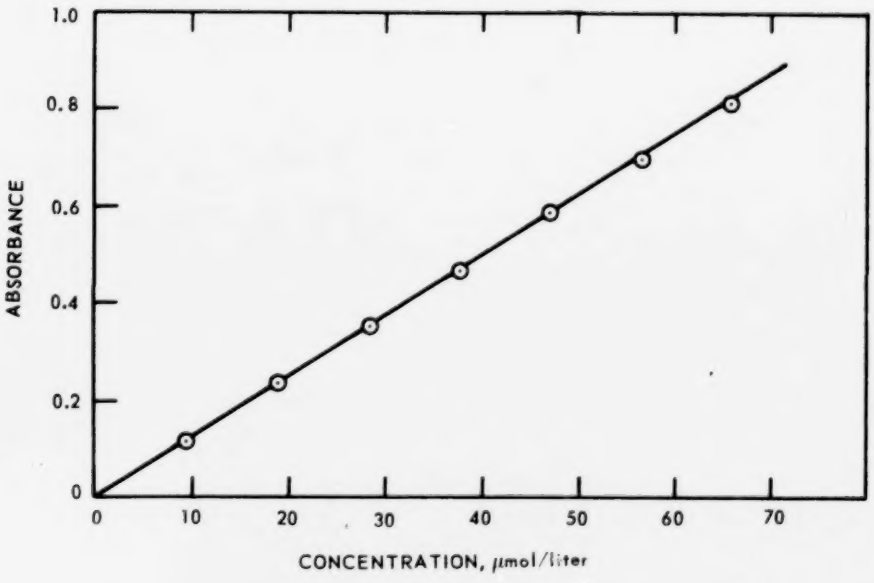

Figure 49. Calibration curve for 2,4,5-trichlorophenoxyacetic acid; cell length 5 cm, λ = 289 mμ.

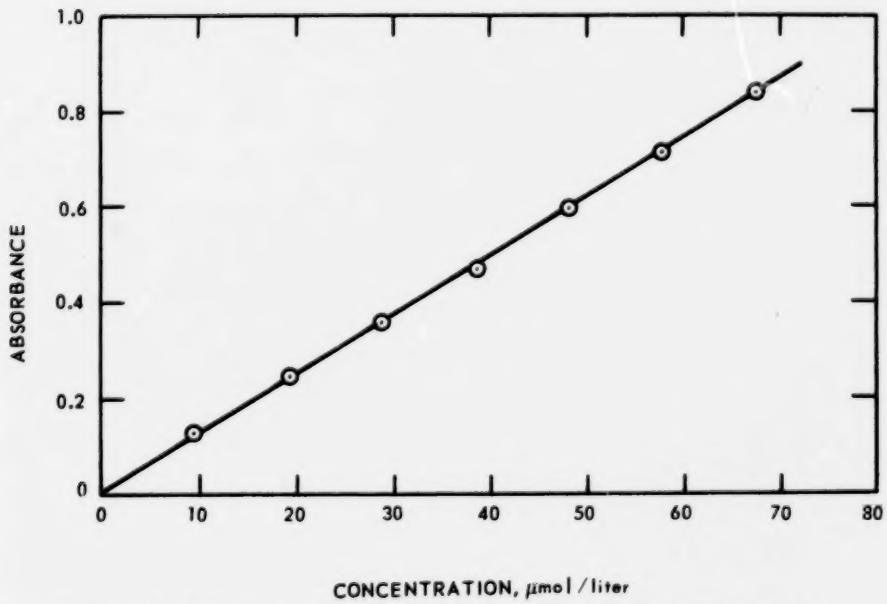

Figure 50. Calibration curve for 2-(2,4,5-trichlorophenoxy)-propionic acid; cell length 5 cm, λ = 289 mμ.

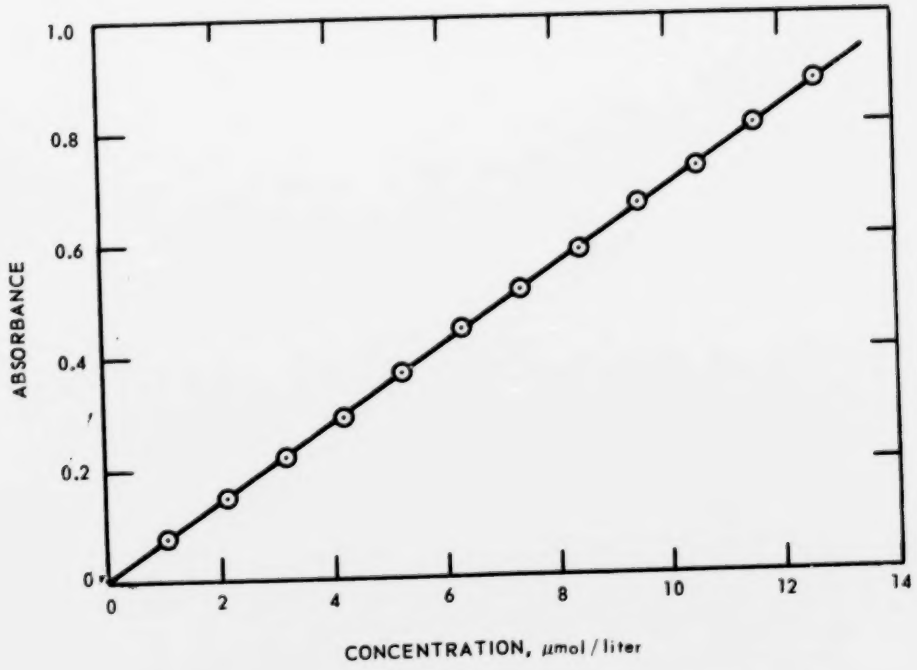

Figure 51. Calibration curve for 2-sec-butyl-4, 6-dinitrophenol; cell length 5 cm, λ = 375 mμ.

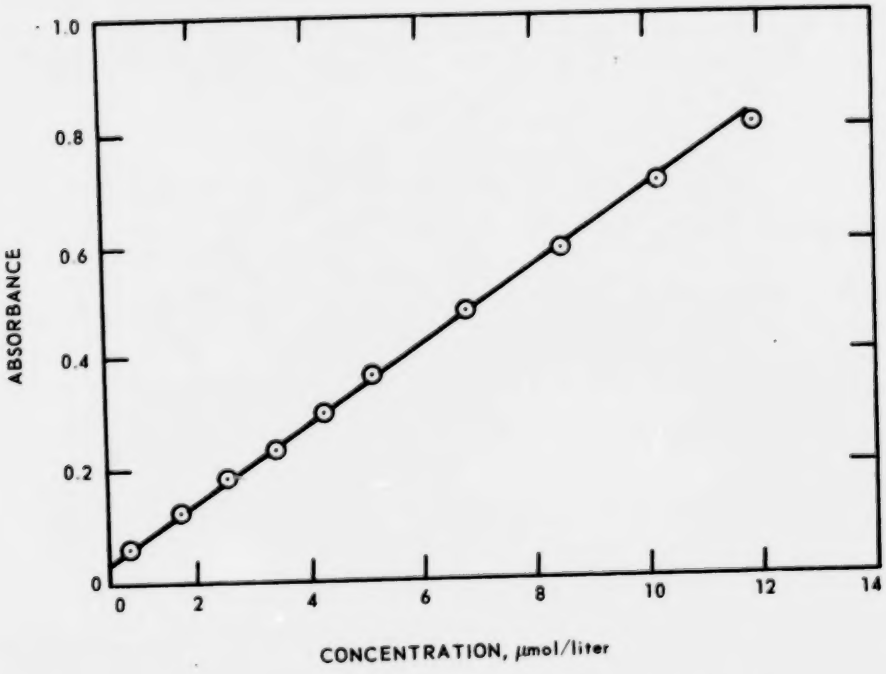

Figure 52. Calibration curve for 2-cyclohexyl-4,6-dinitrophenol; cell length 1 cm, λ = 376 mμ.

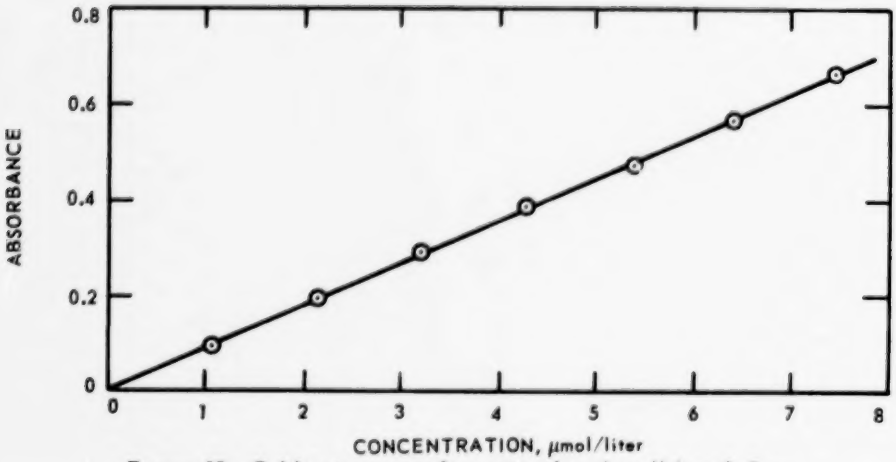

Figure 53. Calibration curve for p-nitrophenol; cell length 5 cm, $\lambda = 400$ mμ.

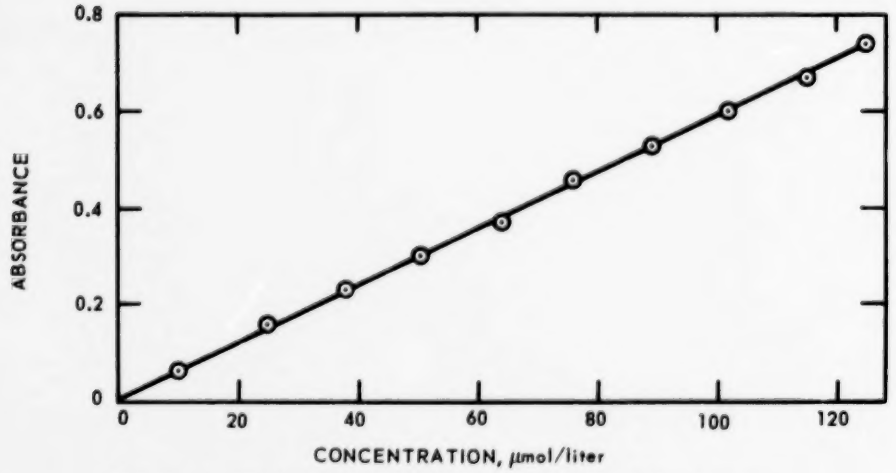

Figure 54. Calibration curve for 1-naphthyl-N-methylcarbamate; cell length 1 cm, $\lambda = 279$ mμ.

EXPERIMENTAL METHODS

Agitated nonflow experiments were used in investigating both the kinetics and equilibria of adsorption of the pesticides on carbon. The batch technique was selected because of its relative simplicity. Advantages of this type of system that figured significantly in its selection were its freedom from complex hydraulic parameters indigenous to flowthrough systems, its adaptability to small-volume work, the ease of investigation of variation of conditions, and the general facility of operation.

Although column operation seems likely to be used for large-scale technical applications of carbon adsorption to waste treatment, evaluation of the fundamental characteristics of adsorption is simpler with a batch technique. Furthermore, once suitable functional relationships for the variables have been established, extrapolation of data from batch

systems to the prediction of behavior in continuous systems should be feasible.

The reaction vessels for the kinetic studies were 4,000-milliliter resistant-glass bottles, in which solutions were agitated with Teflon-coated stirring rods extending directly into the adsorbate solution and connected to synchronous motors operating at 1,550 rpm. Previous kinetic studies in similar systems had shown that the rate of adsorption was independent of stirring rate at rotations greater than a few hundred revolutions per minute.[32] Temperature control for the rate studies was maintained by immersing the reaction vessels in water baths, thermoregulated to 0.5°C. All kinetic studies have been conducted at 28°C.

For each experiment on rate of adsorption, an 8-liter volume of adsorbate solution was prepared at a concentration slightly larger than that desired for the kinetic experiment. Spectrophotometric measurement of the exact concentration of solute in the solution was then made, and the original 8-liter volume diluted appropriately to give more closely a solution of the desired concentration. Exactly 3,000 milliliters of the adjusted solution was then placed in each of two 4-liter reaction vessels. The reaction vessels were then placed in a water bath for approximately 24 hours to allow the solution to attain the desired temperature and to reach adsorptive equilibrium with the surfaces of the vessels. Before introduction of a suitable, accurately weighed quantity of carbon to each vessel, an initial sample was removed and analyzed for concentration of adsorbate. This gave an accurate check on the preparation of the solution and served as the reference concentration for the rate study. The carbon was then introduced into the vessel and rapidly dispersed by the motor-driven stirrer operating at 1,550 rpm. At appropriate intervals the stirring was briefly interrupted while samples of the supernatant solution were pipetted from each of the reaction vessels; the samples for analysis resulted in some small decrease in total adsorbate available to the adsorbent, but the cumulative error of 2 to 3 percent was not significant for this type of experiment. The running of two parallel experiments, identical in all details, provided a check on the reproducibility of the data.

For investigation of adsorptive capacities and equilibria, large volumes of adsorbate solution were prepared and 250 milliliter measures of this solution were dispensed into 300-milliliter resistant-glass reaction flasks. A suitable, accurately weighed amount of adsorbent was then added to each flask, the weight being varied so as to cover the range of equilibrium solute concentrations of interest. For each study, several flasks of solution were left without carbon for use as blanks. The ground-glass-stoppered reaction flasks were then sealed and placed in an oscillating shaker to be shaken for approximately 2 weeks, the times required for equilibrium to be obtained having been determined previously for each type of system. Samples from each of the solutions were analyzed at the end of the appropriate period; the amount of adsorption was computed from the difference between the concentration of adsorbate measured for the blanks and for each reacted solution.

Most studies were conducted in a room maintained at a reasonably uniform temperature, so that fluctuations in the temperatures of the solutions were no more than 2 to 3°C over the duration of the study. The mean temperature for the equilibrium studies was 25°C.

Rates of Adsorption

Previous investigations have indicated that the rate-limiting step for removal of organic solutes from dilute aqueous solution by porous activated carbon in agitated nonflow systems is one of intraparticle transport of the solute in the pores and capillaries of the adsorbent.[32] For systems in which intraparticle transport is the rate-limiting step, data for uptake of solute from solution should give a linear plot as a function of the square-root of time from introduction of the adsorbent to the system.[33] In accord with this method of representing data for systems in which intraparticle transport is the rate-limiting mechanism, the data for the present experiments have been plotted as a function of the square-root of time.

The rate data for the experiments on adsorption of the pesticides on activated carbon are plotted in Figures 55 through 61. The $(C_o-C)/m$ values in these plots represent the amount of solute, both in micromoles and milligrams, removed from solution per gram of carbon. Good linearization of the data is observed for the experiments, in accord with expected behavior for intraparticle-transport rate control. The linear traces facilitate comparison of relative rates of adsorption of the organic pesticides, and this comparison is made in Table 9 by using the square of the slope of each plot as the relative rate constant for the experiment.

Table 9. RELATIVE RATE CONSTANTS FOR ADSORPTION OF ORGANIC PESTICIDES ON CARBON; 28°C, 25 mg/liter 0.273-mm COLUMBIA CARBON, C_o = 10 μmol/liter

Compound	Relative rate constant, k, $[(\mu mol/g)^2/hr] \times 10^{-4}$
2,4-dichlorophenoxyacetic acid	1.44
2,4,5-trichlorophenoxyacetic acid	1.00
2-(2,4,5-trichlorophenoxy)propionic acid	0.71
2-sec-butyl-4,6-dinitrophenol	1.35
2-cyclohexyl-4,6-dinitrophenol	1.12
1-naphthyl N-methylcarbamate	1.64
0,0-diethyl-0-p-nitrophenylphosphorothioate	1.49

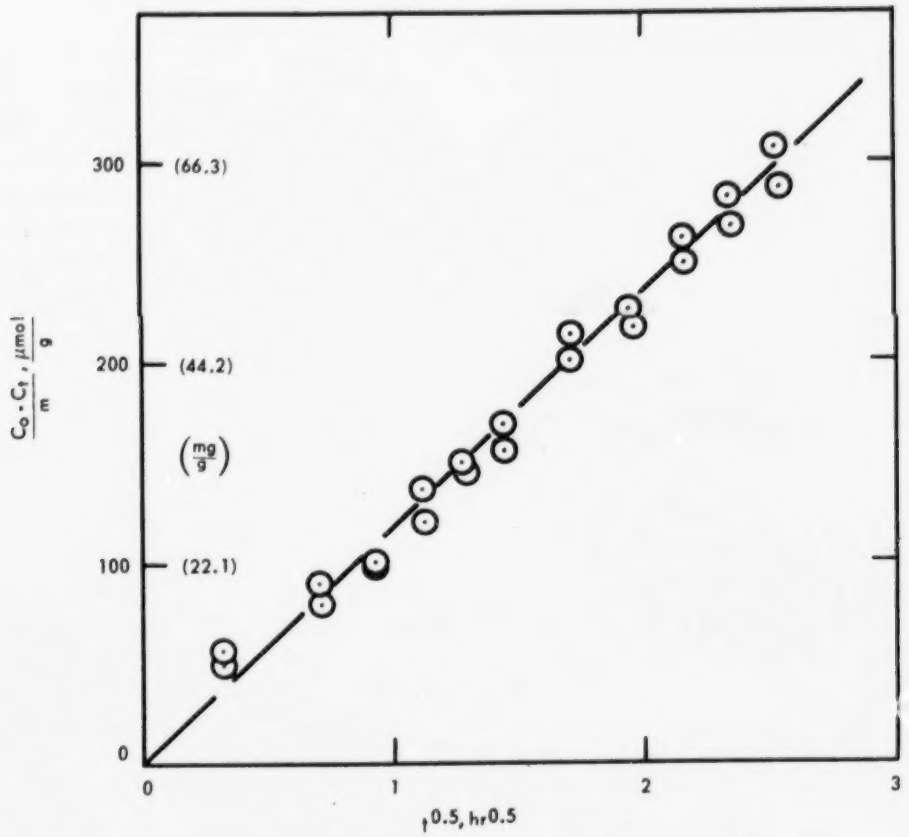

Figure 55. Rate of adsorption of 2, 4-dichlorophenoxyacetic acid.

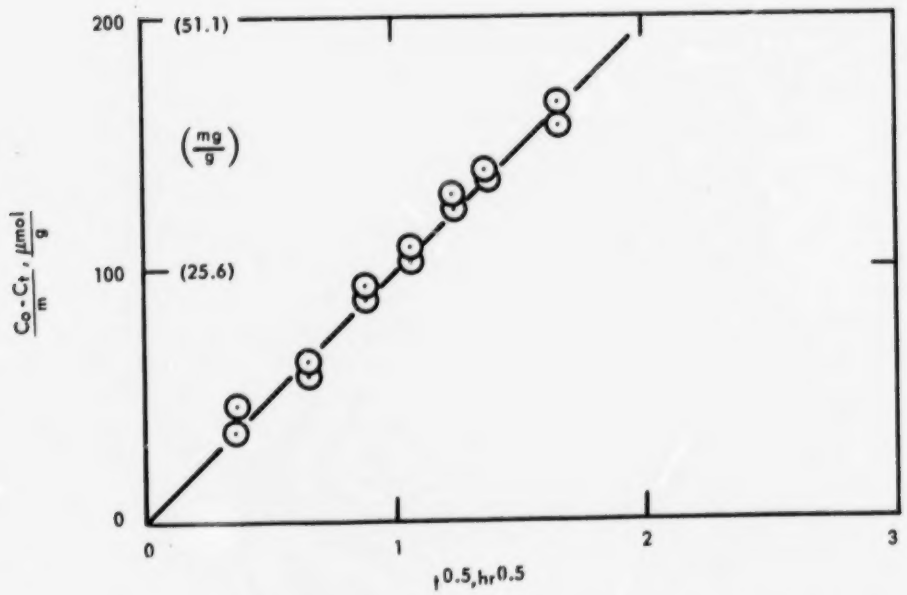

Figure 56. Rate of adsorption of 2,4,5-trichlorophenoxyacetic acid.

Note that the rate constants for adsorption of the various organic pesticides on the 0.273-millimeter carbon are remarkably similar. The data suggest that, even for a rather broad spectrum of different types of organic pesticides, similar rates of removal from solution should obtain. Thus, the effectiveness of activated carbon as related to rate of removal of organic pesticides from solution should be relatively independent of the type of organic pesticide, at least within the classes of compounds and conditions used for the present experiments.

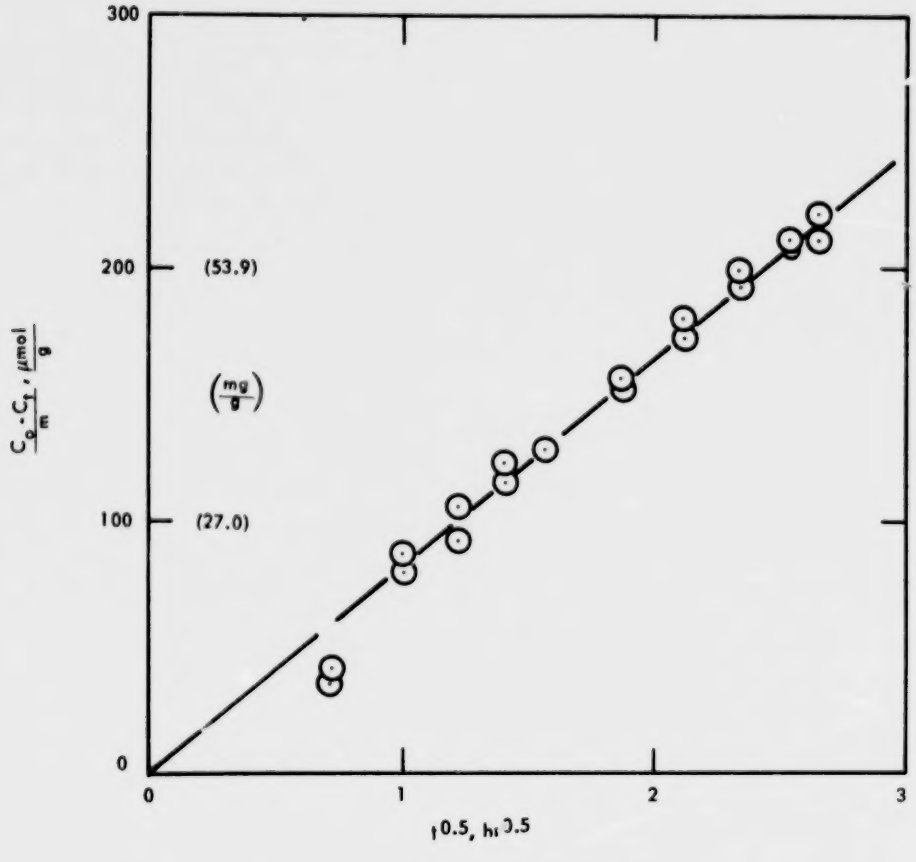

Figure 57. Rate of adsorption of 2-(2,4,5-trichlorophenoxy)-propionic acid.

Concentration of solute in solution was noted to have a significant effect upon the rate of removal by activated carbon. The data shown in Figures 55 through 61 are for experiments conducted with a solution containing initially about 10 micromoles of solute per liter. Figure 62 shows some data for experiments conducted with some of the pesticides at concentrations greater than and slightly smaller than 10 micromoles per liter. The uppermost curve in Figure 62 is for adsorption of 2,4-dichlorophenoxyacetic acid from a solution having an initial concentration of 52.2 micromoles per liter. The middle curve is for 2-(2,4,5-trichlorophenoxy) propionic acid in a solution having an initial concentration of 45.2 micromoles per liter, and the lower curve is for adsorp-

tion of 2-cyclohexyl-4,6-dinitrophenol from a solution with an initial concentration of 7.7 micromoles per liter.

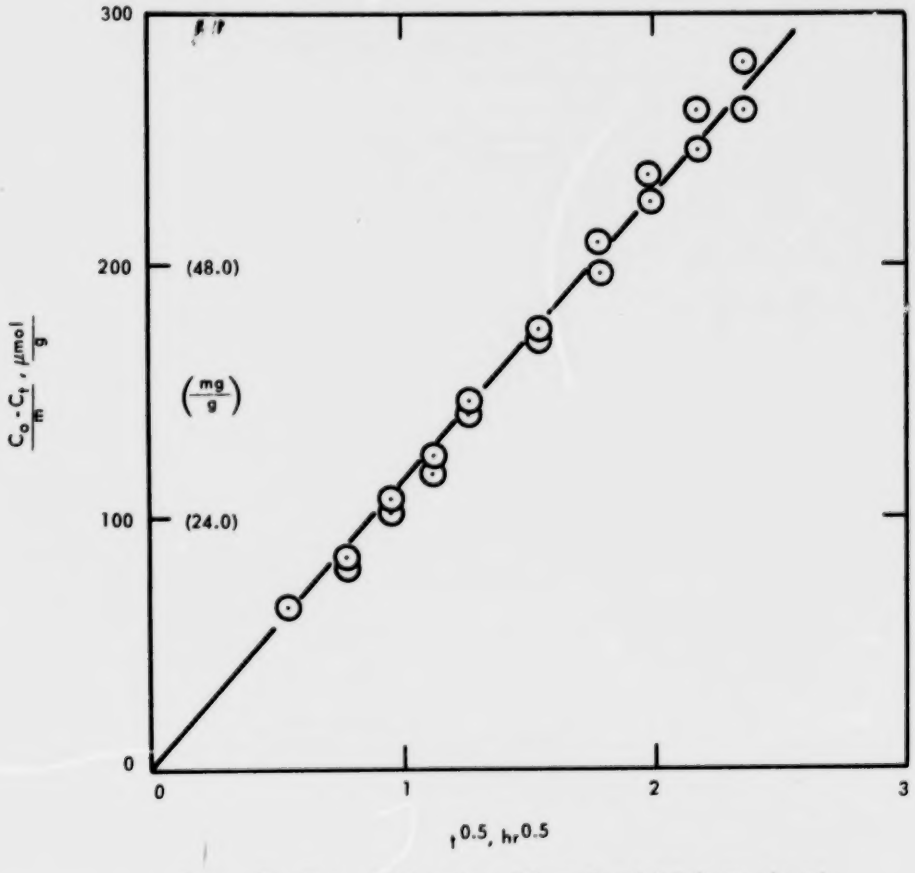

Figure 58. Rate of adsorption of 2-sec-butyl-4,6-dinitrophenol.

For the 2,4-dichlorophenoxyacetic acid, the increase by a factor of 5.1 in the initial molar concentration, over that used in the experiment represented by the data in Figure 55, resulted in a new rate constant of 16.0 x 10^4 (micromoles/gram)^2/hour as compared with a relative rate constant of 1.44 x 10^4(micromoles/gram)^2/hour for the experiment in which the initial concentration was 10.3 micromoles/liter. The experiment at high concentration with 2-(2,4,5-trichlorophenoxy) propionic acid, which represented an increase in initial molar concentration by a factor of 4.6 times that used for the experiment represented by the data in Figure 57, yielded a new relative rate constant of 7.56 x 10^4(micromoles/gram)^2/hour as compared with a value of 0.71 x 10^4 (micromoles/gram)^2/hour, for the experiment with an initial molar concentration of 9.8 micromoles/liter.

Note that the ratio of the relative rate constants for the two solutes, 2,4-dichlorophenoxyacetic acid and 2-(2,4,5-trichlorophenoxy) propionic

acid, obtained from the experiments at small concentration is 2.03, while the ratio of the relative rate constants obtained from the experiments at the large concentrations is 2.11. Apparently, therefore, the effect of initial concentration upon the rate at which organic pesticides are removed from water by activated carbon is relatively uniform, at least for similar classes of organic pesticides.

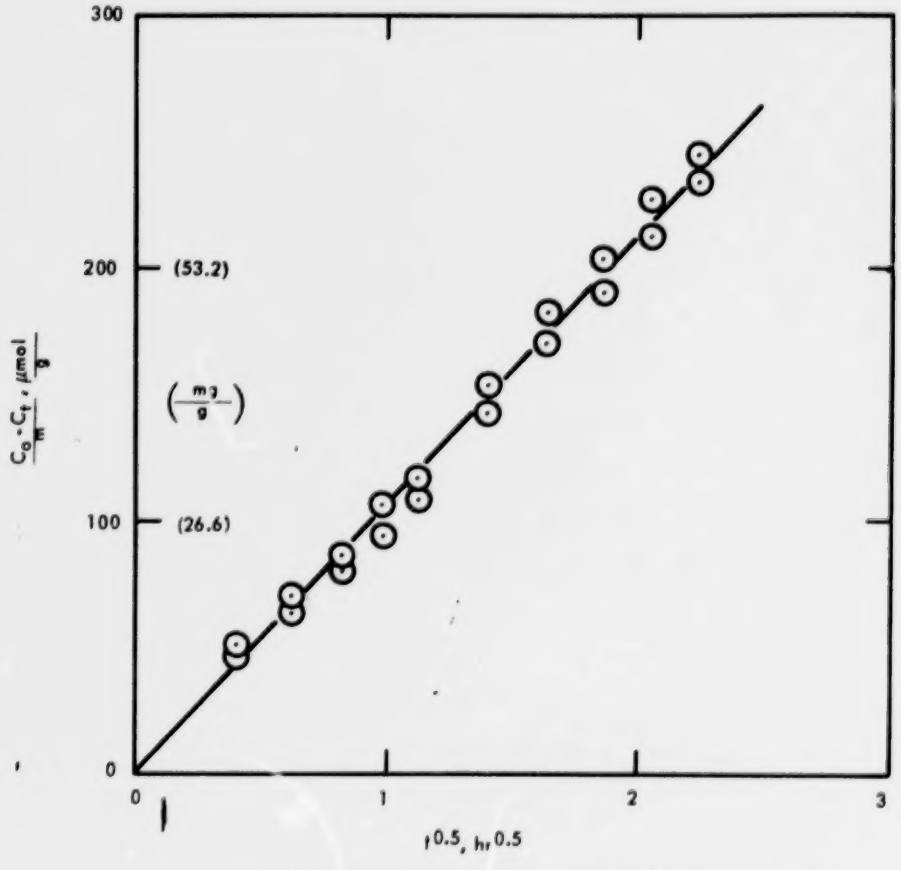

Figure 59. Rate of adsorption of 2-cyclohexyl-4,6-dinitrophenol.

The relative rate constant for the 2-cyclohexyl-4,6-dinitrophenol obtained from the experiment with an initial molar concentration of 7.7 micromoles per liter was 0.90 x 10^4(micromoles/gram)^2/hour as compared with a value of 1.12 x 10^4(micromoles/gram)^2/hour obtained for the experiment with an initial molar concentration of 10.2 micromoles/liter. Thus the effect of initial concentration appears qualitatively uniform for different classes of organic pesticides.

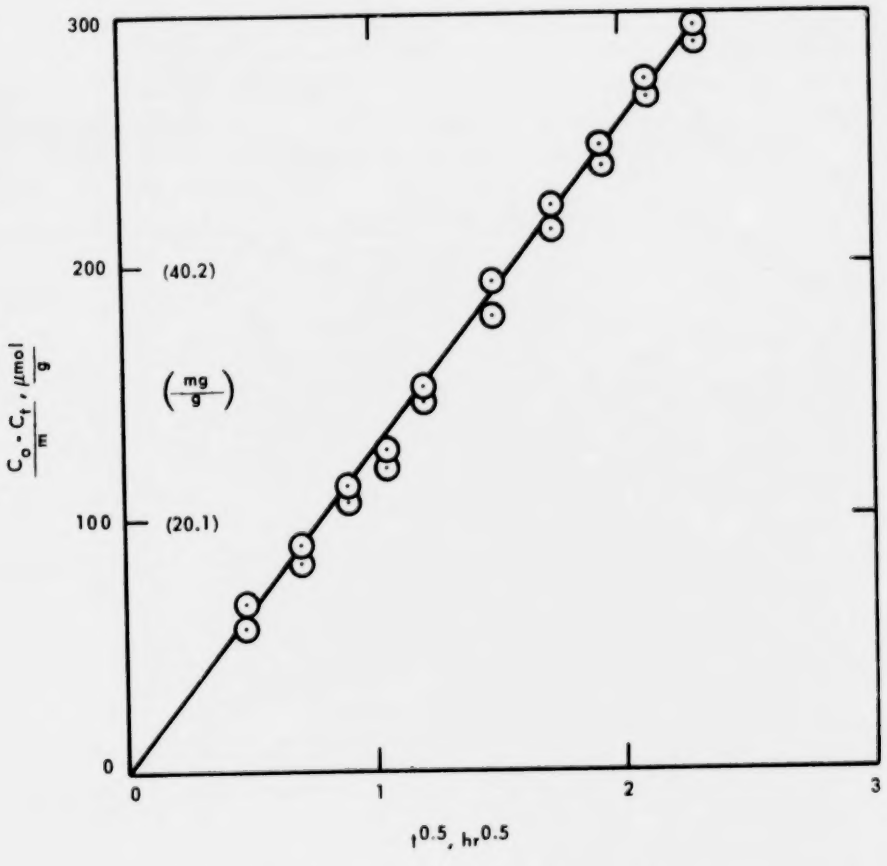

Figure 60. Rate of adsorption of 1-naphthyl-N-methylcarbamate.

Adsorption Equilibria

The extent to which the full surface area of an activated carbon can be used for adsorption depends on the concentration of solute in the solution with which the carbon is mixed. The specific relationship between concentration of solute and the degree of its removal from solution by an adsorbent at constant temperature and for conditions of equilibrium defines the adsorption isotherm. The preferred form for representing the adsorption isotherm is to express the quantity of solute adsorbed per unit weight of adsorbent as a function of C, the equilibrium concentration of solute remaining in solution.

A number of different types of adsorption relationships may obtain under different circumstances. The most common relationship between the amount of solute adsorbed per unit of adsorbent and the equilibrium concentration in solution is obtained for systems in which it appears that adsorption from solution leads to the deposition of only a single layer

of solute molecules on the surface of the solid. This type of adsorption equilibrium is best represented by the Langmuir model for adsorption, which assumes that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no movement of adsorbate molecules in the plane of the surface after initial adsorption.[34]

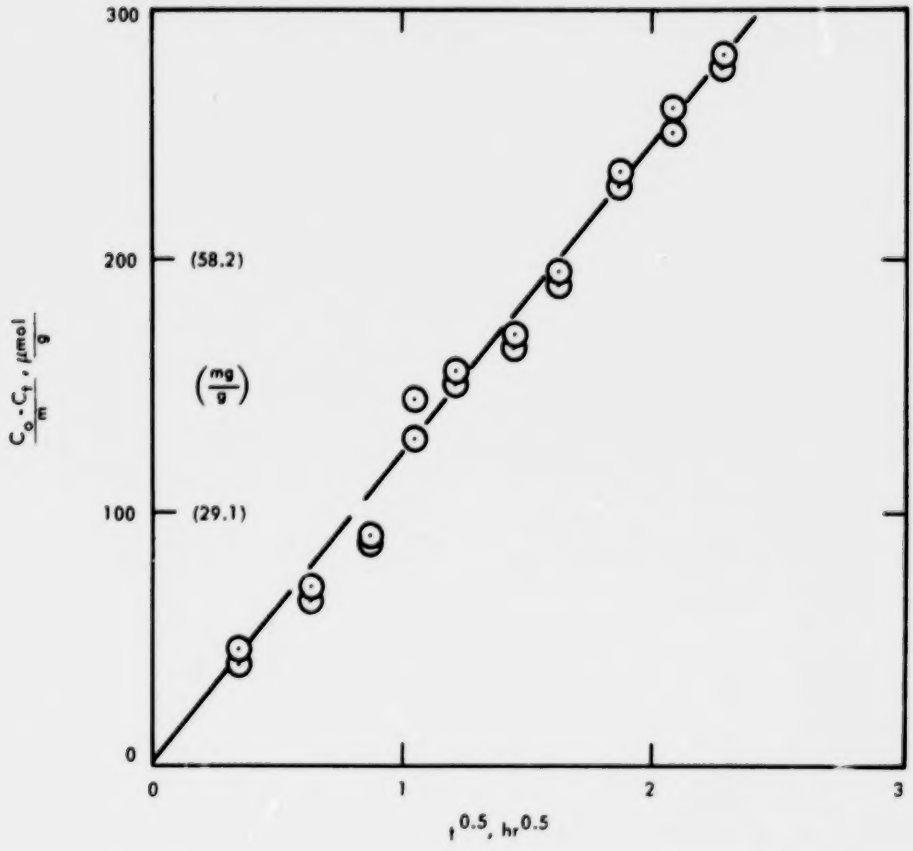

Figure 61. Rate of adsorption of 0, 0-diethyl-0-p-nitrophenol.

The form of the Langmuir adsorption isotherm is

$$X = \frac{X_m bC}{1 + bC} \qquad (12)$$

in which C indicates the measured concentration in solution at equilibrium, X_m is equal to the number of moles of solute per gram of carbon adsorbed in forming a complete monolayer on the carbon surface, X represents the number of moles of solute adsorbed per gram of carbon at concentration C, and b denotes a constant related to the energy of adsorption. The reciprocal, 1/b, is the concentration at which adsorption attains half its limiting X_m value.

Two convenient linear forms for the Langmuir equation are:[34]

$$\frac{1}{\overline{X}} = \frac{1}{X_m} + \frac{1}{bX_mC} \tag{13}$$

and

$$\frac{C}{\overline{X}} = \frac{1}{bX_m} + \frac{C}{X_m} \tag{14}$$

Either Equation 13 or 14 may be used for linearization of data that conform to the Langmuir equation. The form chosen usually depends on the range and spread of the data and on the particular range of data to be emphasized.

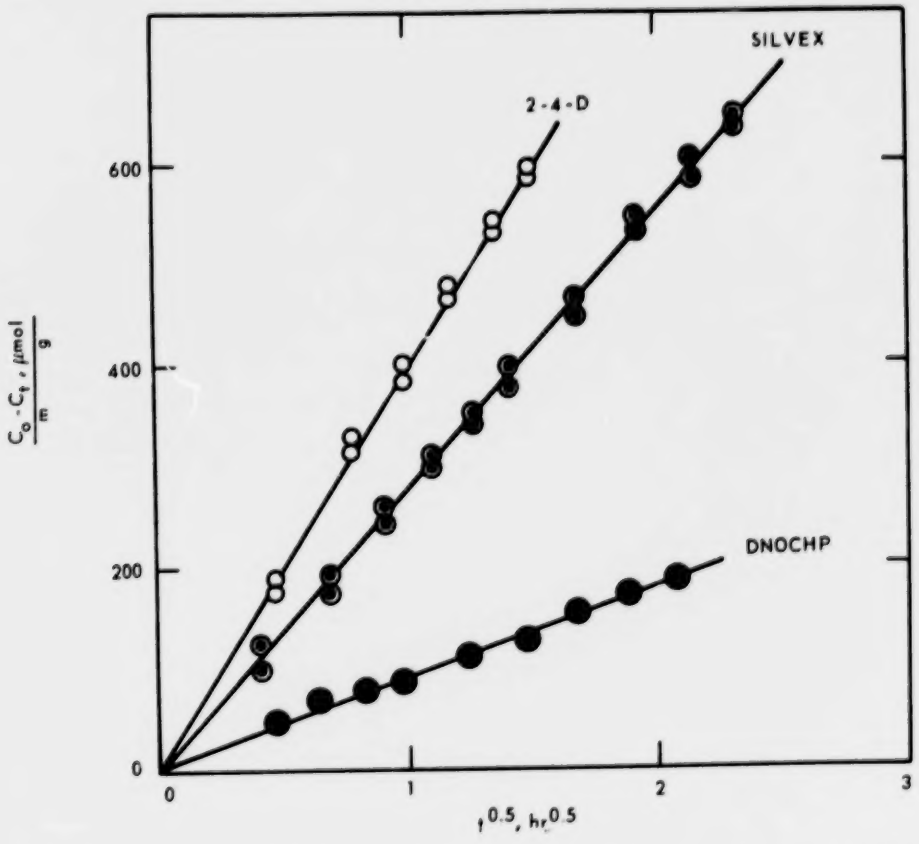

Figure 62. Rates of adsorption of 2, 1-dichlorophenoxyacetic acid, 2-(2,4,5-trichlorophenoxy) propionic acid, and 2 -cyclohexyl-4,6-dinitrophenol from solutions of different initial concentration.

All the organic pesticides tested exhibit equilibrium adsorption on the experimental carbon in reasonable accord with the Langmuir model for adsorption. The data for isothermal equilibrium adsorption experiments are plotted in Figures 63 through 68. The points on these plots are the experimental data; the solid curves through the points are calculated Langmuir adsorption isotherms. Figures 69 through 74 are linear plots of the data according to the linear form of the Langmuir

adsorption isotherm given by Equation 13. The intercept, with the ordinate, of each line drawn through the data in Figures 69 thru 74 represents the reciprocal of the ultimate capacity for adsorption, $\frac{1}{X}$, and the slope of each plot represents the reciprocal of bX_m. From the intercepts and slopes of the linear Langmuir plots, values for the Langmuir constants for each solute have been calculated; these values for the Langmuir parameters are listed in Table 10.

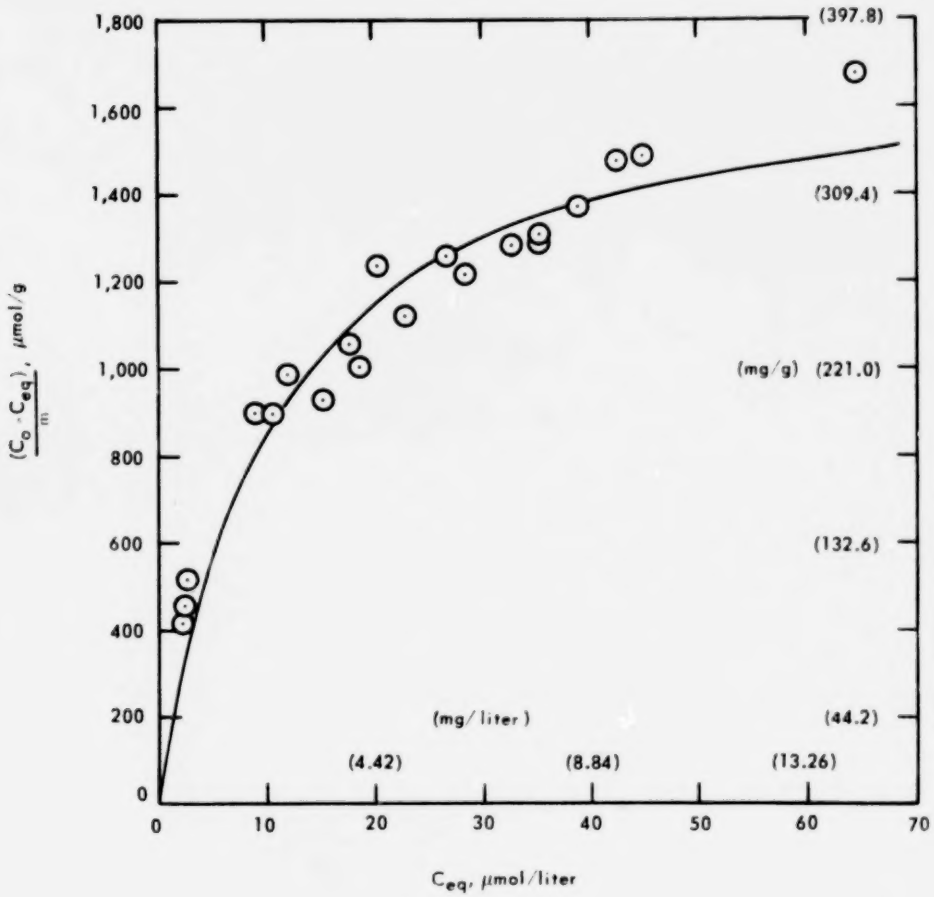

Figure 63. Adsorption isotherm for 2,4-dichlorophenoxyacetic acid.

As was the case for the relative rate constants for the different organic pesticides, values of X_m, listed in Table 10, are similar in magnitude for the different adsorbates, on the order of 1,800 micromoles of solute per gram of carbon. Thus, the ultimate capacity appears to be relatively independent of the type of organic pesticide tested, at least within the experimental ranges. With the exception of the Parathion, values for the parameter b, which is a measure of the energy of adsorption, are similar for the organic pesticides. The fact that the value for b for the Parathion is an order of magnitude higher

Table 10. LANGMUIR CONSTANTS FOR ADSORPTION ISOTHERMS OF PESTICIDES ON ACTIVATED CARBON; 25°C, 0.273-mm COLUMBIA LC CARBON

Compound	X_m, (μmol/g)x 10^{-3}	b, (1/μmol)
2,4-dichlorophenoxyacetic acid	1.75	0.095
2,4,5-trichlorophenoxyacetic acid	1.75	0.150
2-(2,4,5-trichlorophenoxy) propionic acid	1.72	0.145
2-sec-butyl-4,6-dinitrophenol	1.85	0.174
2-cyclohexyl-4,6-dinitrophenol	1.88	0.148
0,0-diethyl-0-p-nitrophenyl phosphorothiate	1.82	1.22

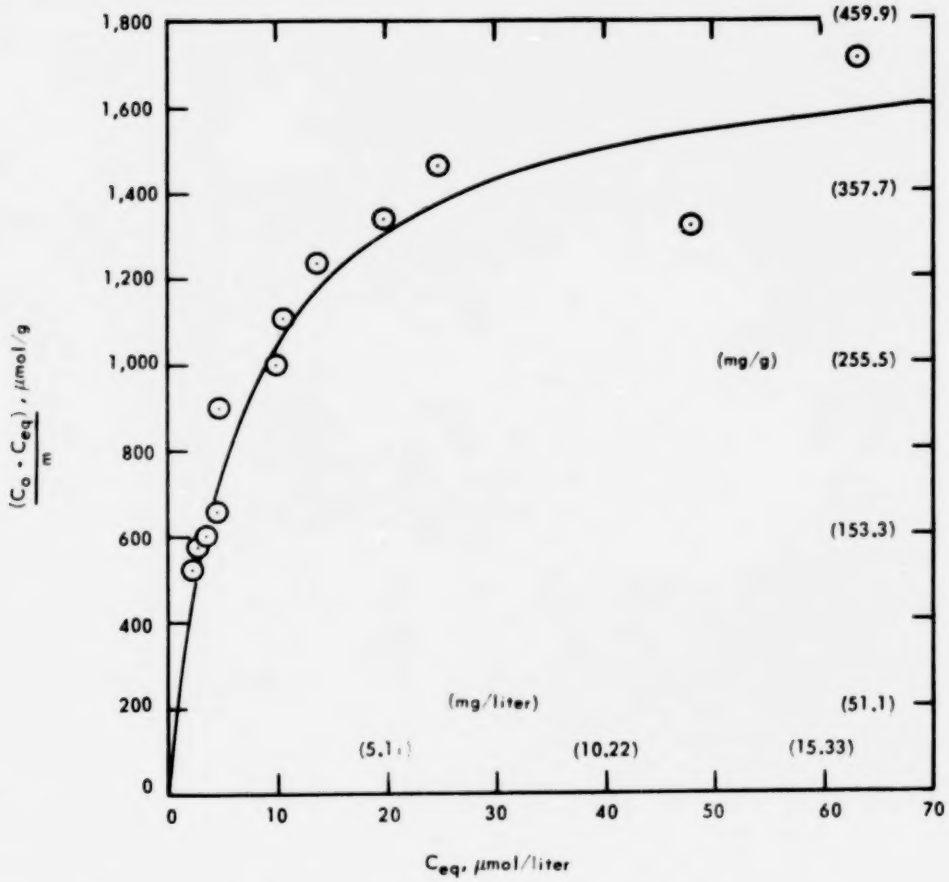

Figure 64. Adsorption isotherm for 2,4,5-trichlorophenoxyacetic acid.

than values of b for the other organic pesticides indicates that this material has a high energy of adsorption and attains adsorptive capacities near the ultimate capacity at relatively small equilibrium concentrations of solute in solution.

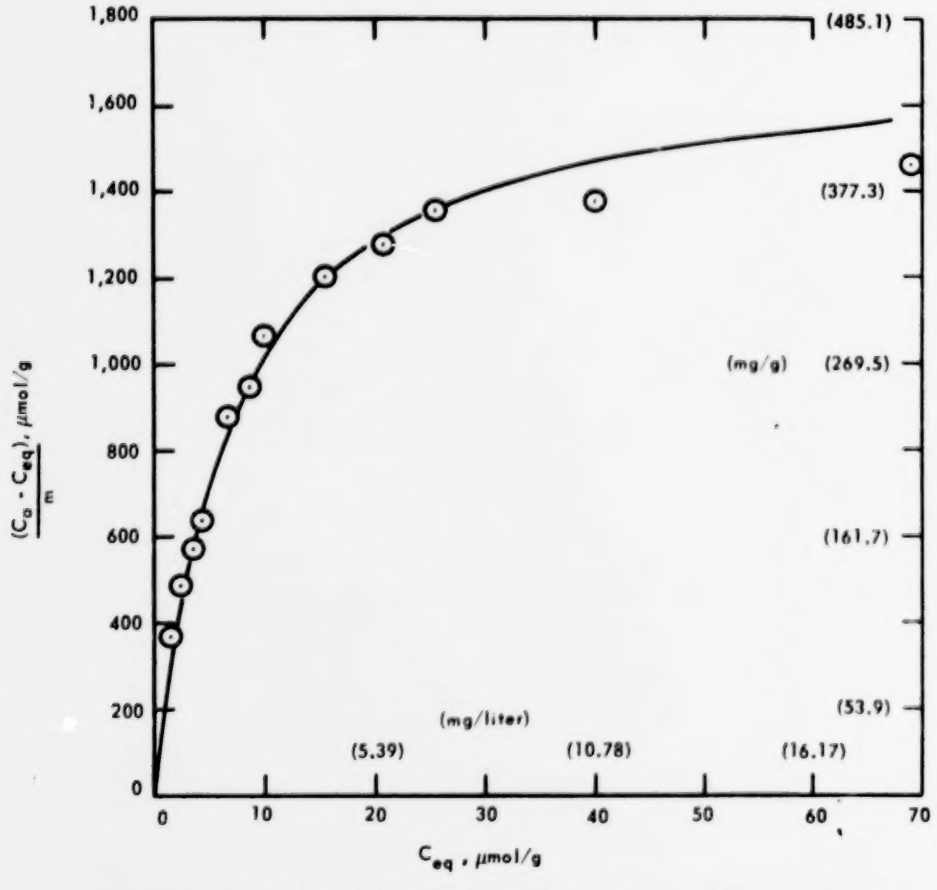

Figure 65. Adsorption isotherm for 2-(2,4,5-trichlorophenoxy)-propionic acid.

Comparison may also be made between the values of X_m and of b obtained with these pesticides and those obtained earlier for ABS and other compounds. Results of some of these earlier studies along with those for the pesticides are shown in Table 11 with somewhat different units than those given in Table 10.

The capacity values for the pesticides are very large, even greater on a weight basis than that previously reported for p-nitrochlorobenzene. On the other hand, the 1/b values, except for that of Parathion, indicate approach to the saturation adsorption only at relatively large residual concentrations of the adsorbate.

The capacity figures are probably the most significant for column operation, for countercurrent operation makes realizable capacities

Table 11. COMPARISON OF LANGMUIR CONSTANTS FOR VARIOUS ADSORBATES ON ACTIVATED CARBON

Compound	X_m, mmol/g	X_m, mg/g	1/b, μmol/liter	1/b, mg/liter
2,4-D	1.75	387	10.5	2.32
2,4,5-T	1.75	448	6.7	1.71
Silvex	1.72	464	6.9	1.86
DNOSBP	1.85	444	5.8	1.39
DNOCHP	1.88	500	6.8	1.81
Parathion	1.82	530	0.82	0.24
Phenol	1.09	103	9.3	0.87
2-dodecylbenzenesulfonate	0.40	139	0.22	0.078
1-chloro-4-nitrobenzene	2.52	400	1.4	0.22

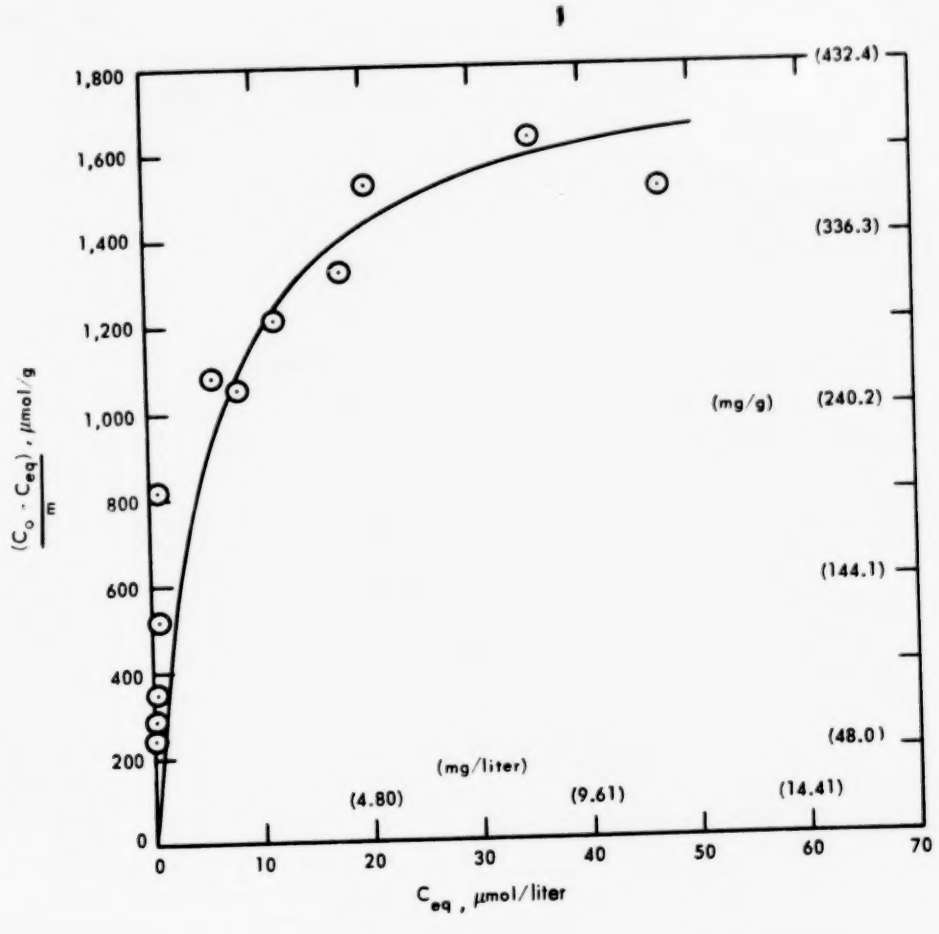

Figure 66. Adsorption isotherm for 2-sec-butyl-4,6-dinitrophenol.

those corresponding to initial concentrations rather than to allowable effluent concentrations. The 1/b values give an indication of the anticipated sharpness of the breakthrough front and to some extent provide guidance for the optimum depth of column for satisfactory removal of the contaminant, although rate of adsorption is an equally important factor in this respect. Larger 1/b values in general would call for greater depths of adsorption column.

Analysis of this type can give only very qualitative conclusions with regard to the pesticides, for obviously, the basic assumption of the Langmuir treatment, that only a monomolecular layer of adsorbed material is formed, does not hold when one is considering weights of adsorbed material in the neighborhood of 40 percent of the weight of adsorbent. While the Langmuir formulation does provide an adequate representation of the data for adsorptive equilibrium over a large and relatively high concentration range, it seems likely that more refined experimentation in a smaller concentration range (say 1 to 100 ppb) would show considerably greater adsorption of the pesticides than that predicted by the Langmuir constants presented here. Indeed, the experimental results for the lower end of the concentration range shown in Figures 66 and 67 provide some evidence of this. Two different Langmuir formulations may be needed for more exact description such as those found for phenol in smaller and larger ranges of concentration. There the value of X_m at larger concentrations was found to be 3.32 millimoles per gram or 310 milligrams per gram rather than the figures recorded in Table 11. Note that the phenol concentrations giving the higher capacity were from 6 to 14 percent of the saturation values in water. Many of the pesticides were studied in about this range of fractional concentrations of their saturation values.

Consequently, cleanup of small concentrations of pesticides by activated carbon seems likely to be considerably more efficient than indicated by the Langmuir constants obtained in these studies. Problems of initial leakage of these materials are not expected to occur when beds of adequate depth (5 to 10 ft) of activated carbon are used for advanced waste treatment.

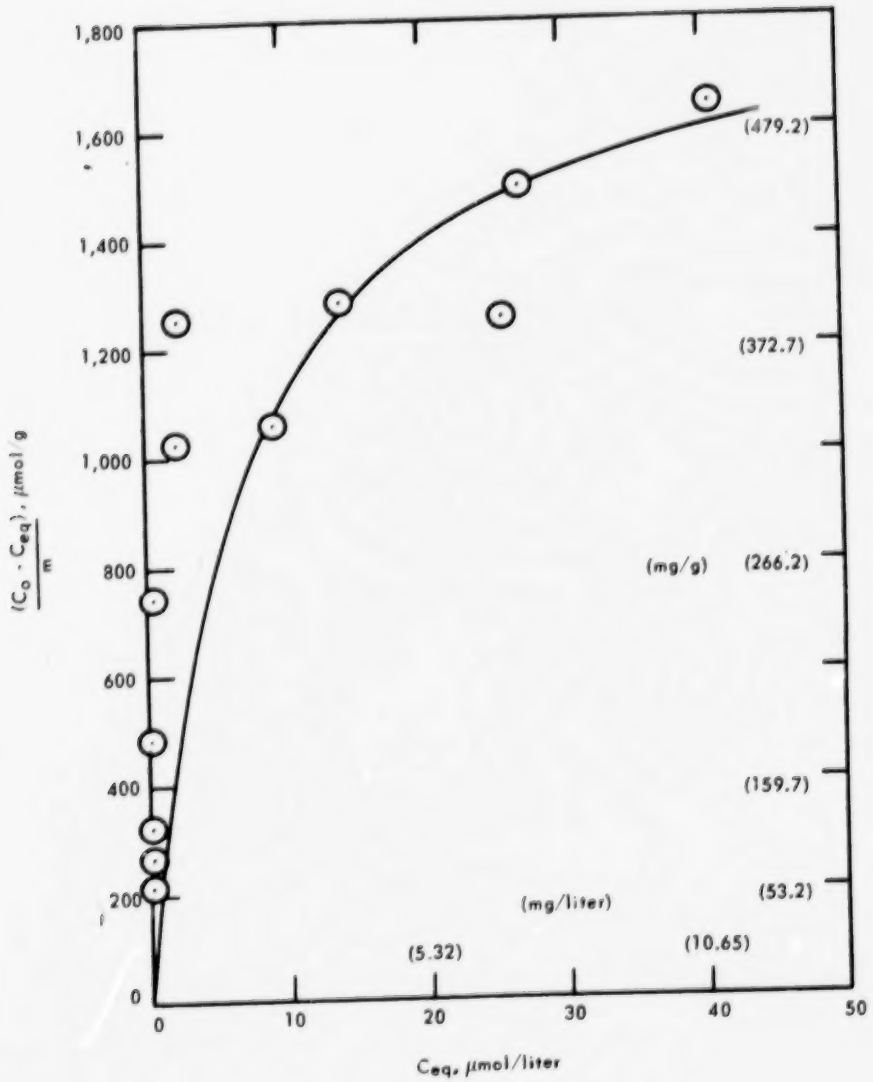

Figure 67. Adsorption isotherm for 2-cyclohexyl-4, 6-dinitrophenol.

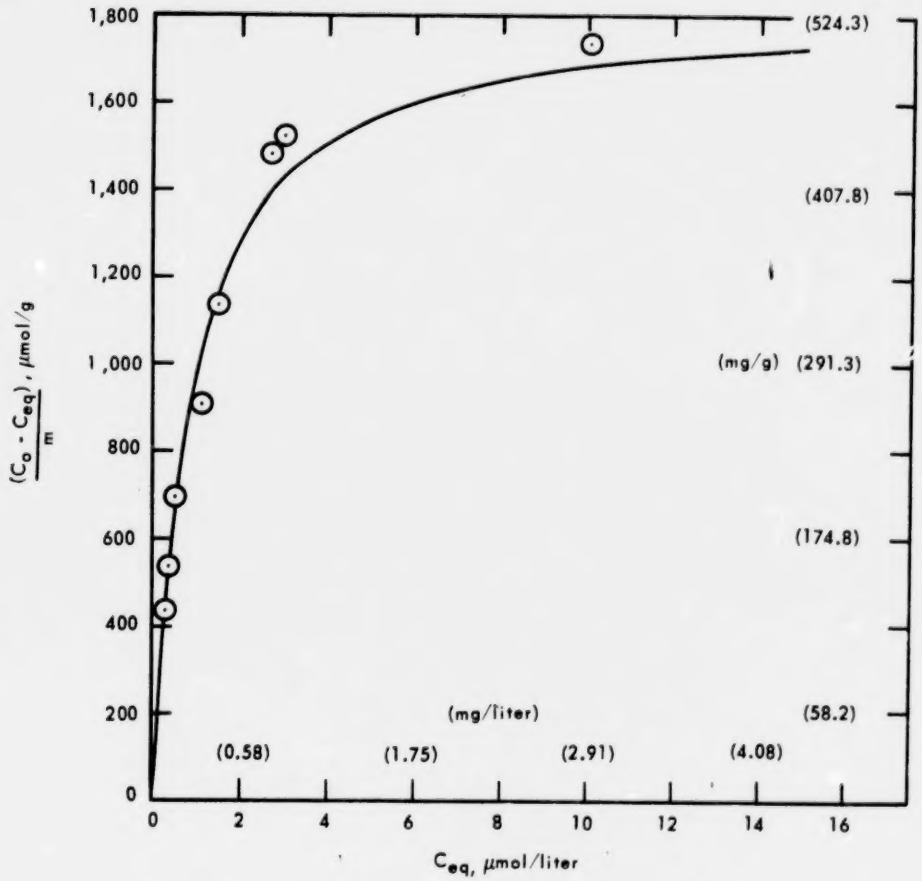

Figure 68. Adsorption isotherm for 0,0-diethyl-0-p-nitrophenol-phosphorothioate.

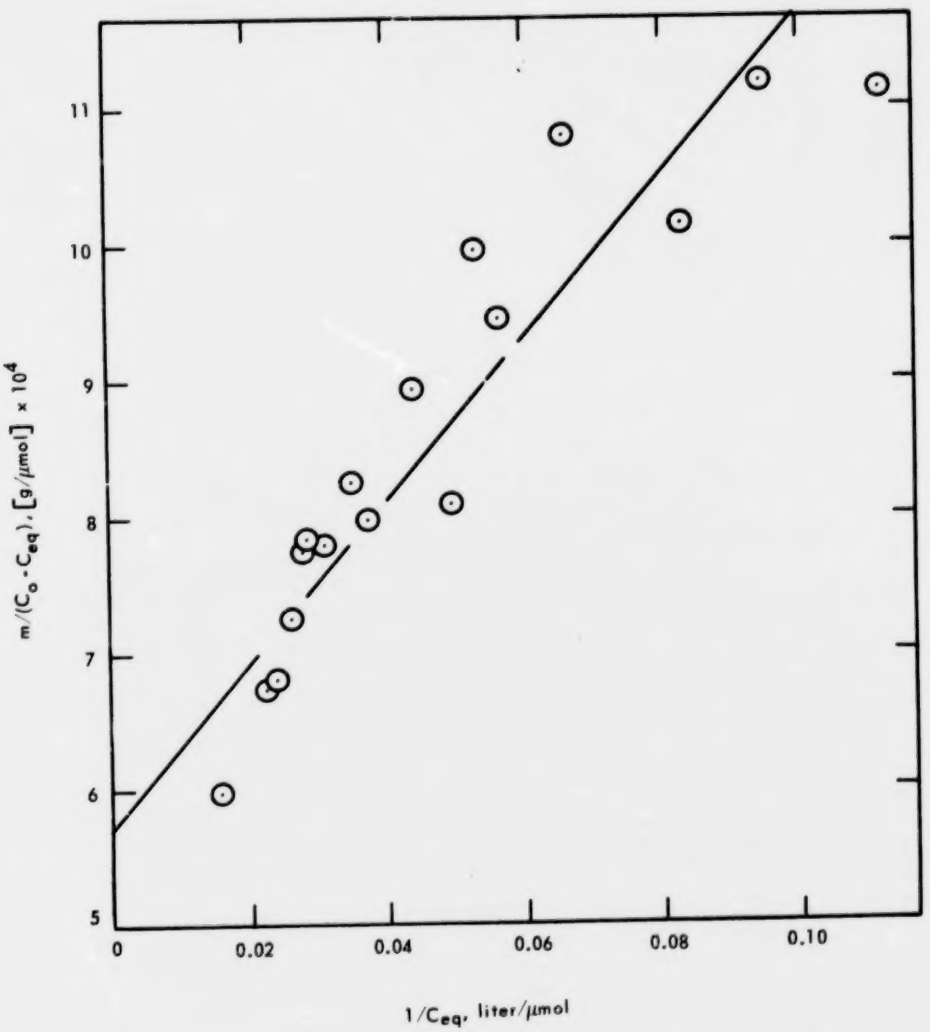

Figure 69. Langmuir plot for 2,4-dichlorophenoxyacetic acid.

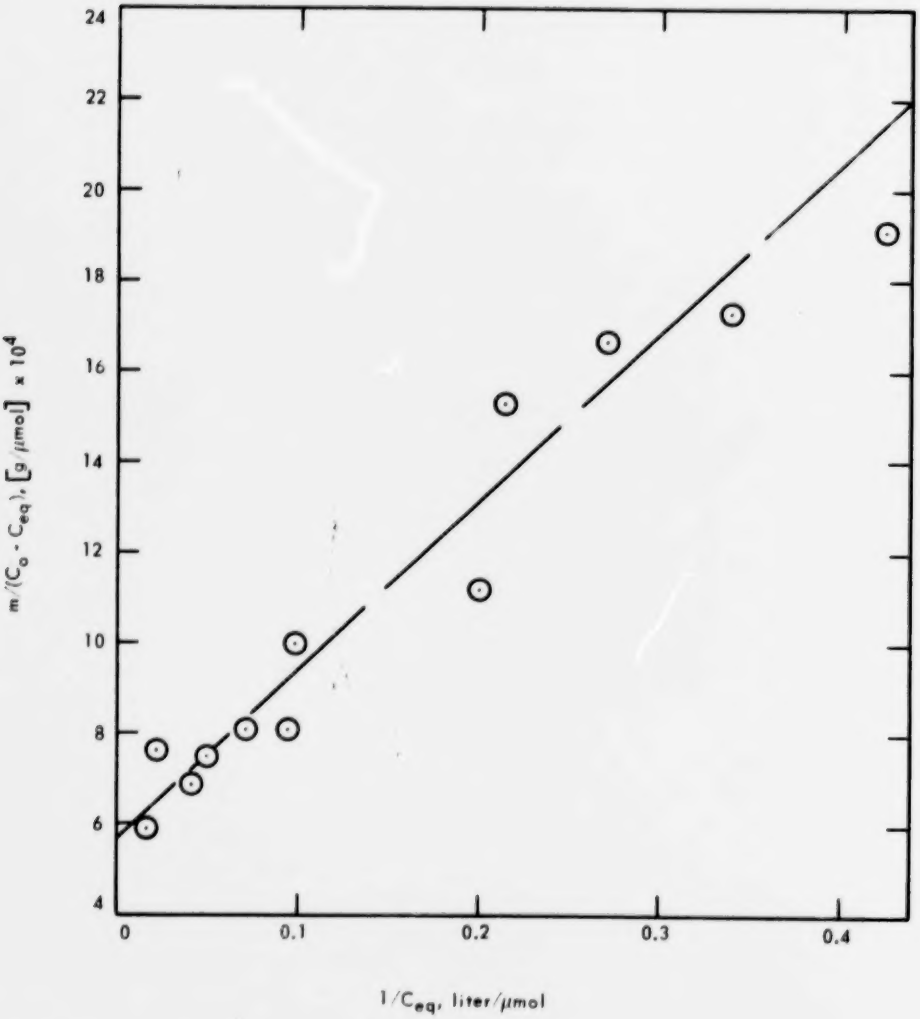

Figure 70. Langmuir plot for 2,4,5-trichlorophenoxyacetic acid.

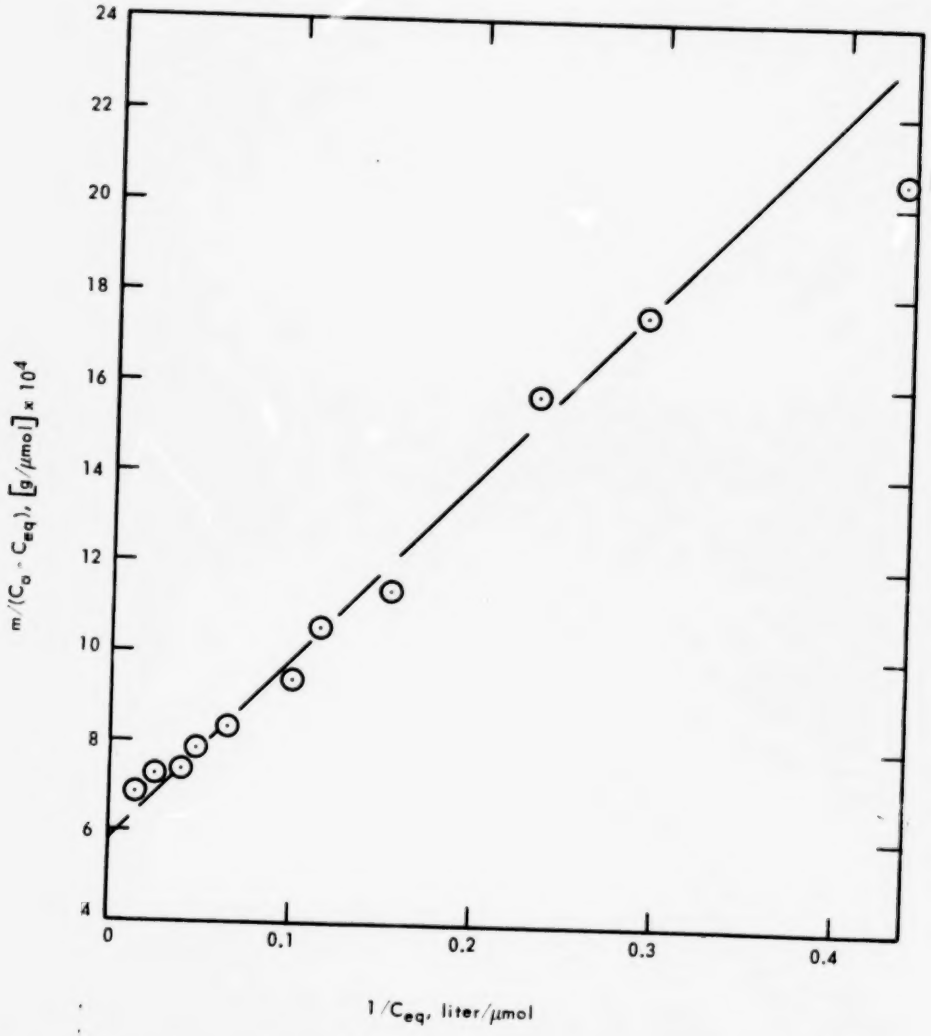

Figure 71. Langmuir plot for 2-(2,4,5-trichlorophenoxy)-propionic acid.

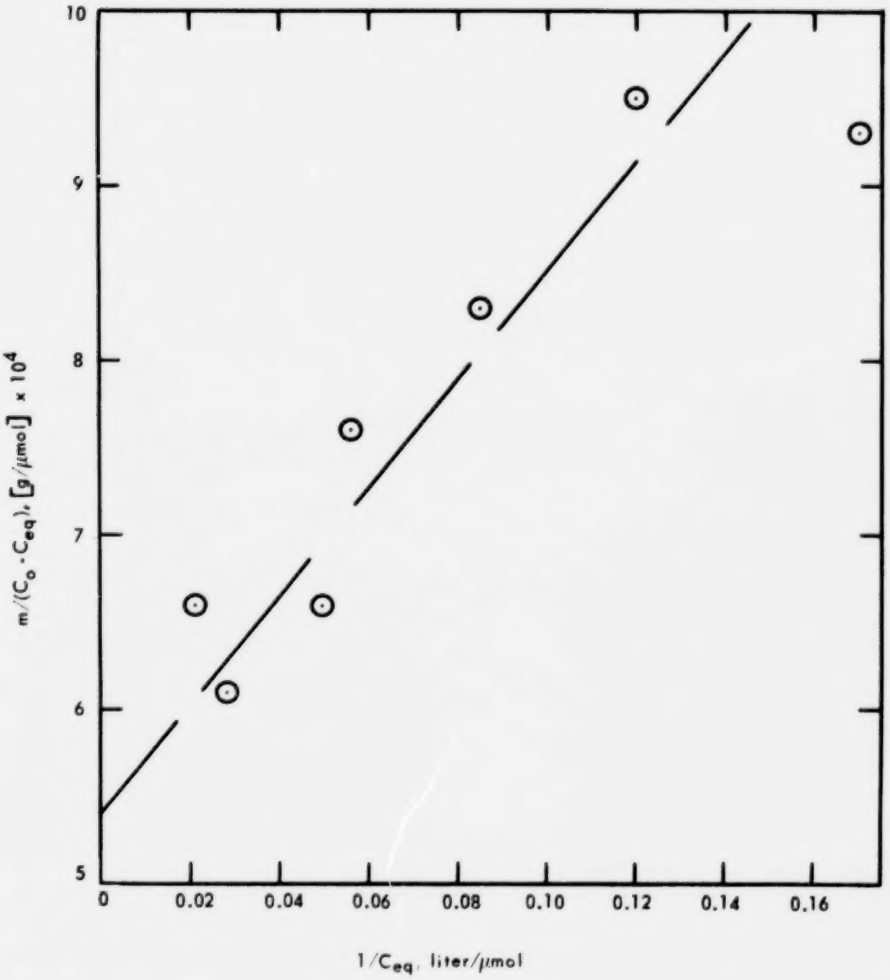

Figure 72. Langmuir plot for 2-sec-butyl-4,6-dinitrophenol.

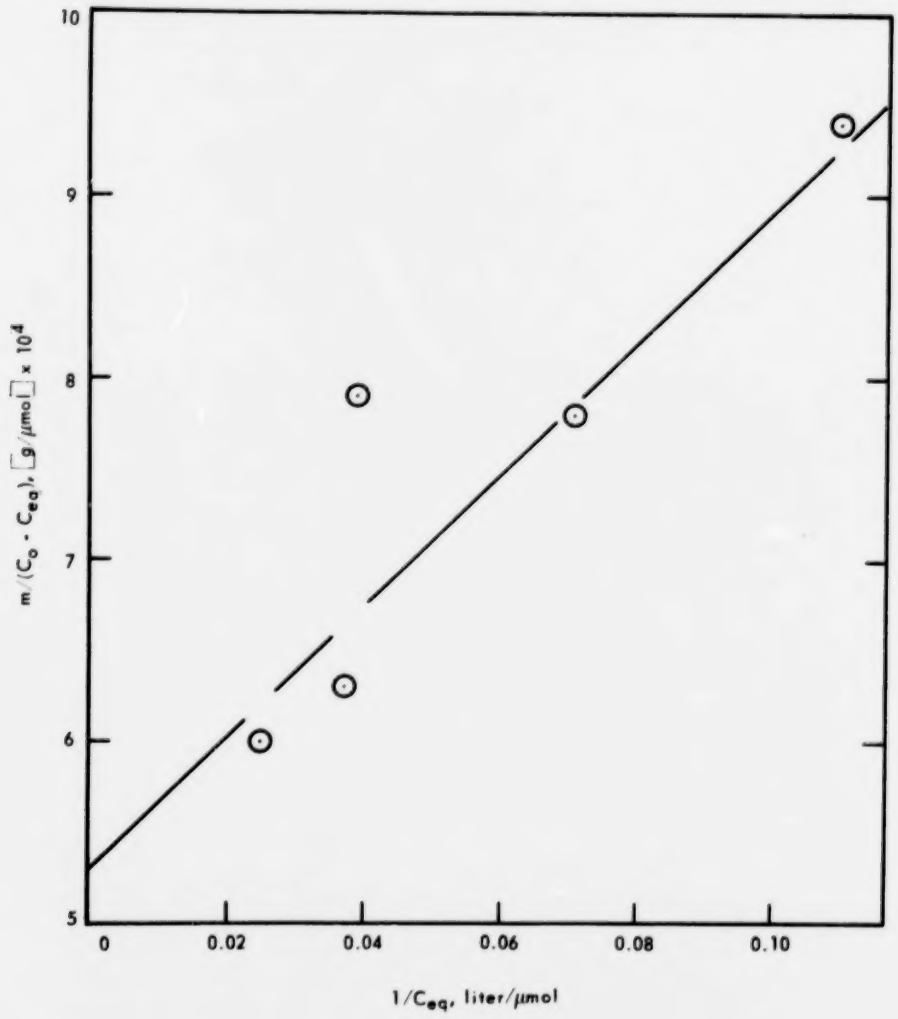

Figure 73. Langmuir plot for 2-cyclohexyl-4,6-dinitrophenol.

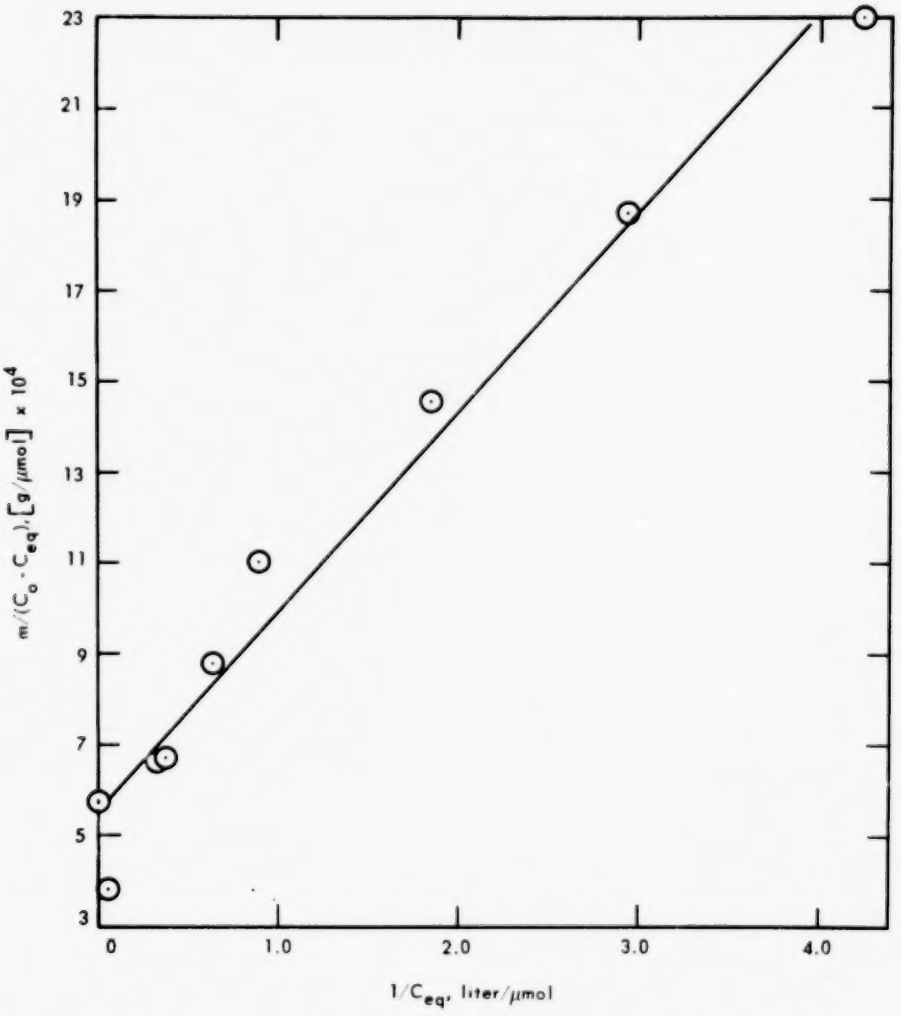

Figure 74. Langmuir plot for 0,0-diethyl-0-p-nitrophenol.

EXAMINATION OF EFFLUENTS FROM ACTIVATED CARBON COLUMNS

Studies on the removal of residual organic pollutants from conventionally treated sewage by means of activated carbon have indicated that there is initial leakage of organic material regardless of the extent of carbon treatment.[35] These studies at the Pittsburgh Chemical Company involved conventional filtration of secondary sewage effluents through beds of granular activated carbon 5 feet in depth, one to four of these units being used in series. Leakage of organic material was measured as chemical oxygen demand in the effluents and was found to be substantially the same after passage through four units as after filtration through a single unit.

The nature of the unadsorbed organic material was not known and is difficult to determine because of the small total concentration and the variety of possible components.

Nonetheless, obtaining some idea of the types of substances not effectively removed by carbon adsorption is of great importance. If these are compounds that have great hygienic significance, then the value of adsorption on carbon as a method for advanced waste treatment is seriously diminished. On the other hand, if they are normal bacterial metabolites that have escaped oxidation during conventional sewage treatment, or similar compounds, then their presence in small quantity may not represent a significant degradation in effluent quality.

It seemed possible that useful information on the nature of the organic materials might be obtained after concentration of effluent by vacuum distillation. Such treatment would change the effluent by loss of volatile constituents, but these are not likely to be of importance. Other changes that might occur or their effects are more difficult to assess, but any thermal changes should be minimized by concentrating at as low a temperature as possible.

Accordingly, samples of effluent from the carbon columns of the Pittsburgh studies were concentrated by vacuum evaporation at the R.A. Taft Sanitary Engineering Center, and two of the concentrates were then shipped to Harvard for examination. Sample number one, dated February 7, 1964, had been concentrated by a factor of 36:1, and sample number two, dated May 5, 1964, had been concentrated by a factor 60:1.

Because of limitations of time, not nearly as much was done with these samples as would have been desirable. Besides very general tests, only a few determinations of specific types of substances were attempted, and the results of these had more significance in a negative

sense than in a positive one. Nonetheless, it is believed that the methods of approach have value and that more extensive and detailed examination of similar concentrated effluents from carbon columns should be undertaken by others.

The concentrated effluents as received contained considerable sediment. Much of this was inorganic material such as $CaCO_3$ and $CaSO_4$ that had precipitated during the evaporation. Some organic matter, however, had also coagulated or precipitated to such an extent that it was removable by filtration through a membrane filter. This may indicate that a part of the organic matter leaking through the columns is colloidal and perhaps, therefore is either carbohydrate or protein. It would be desirable to pass some unconcentrated effluent through a Seitz or other molecular filter to see how much of the effluent COD would be removed by such treatment. Presumably material of the types indicated would not be particularly deleterious.

Note also that sample number one exhibited rapid growth of microorganisms both during shipment and after receipt. Such growth implies that much of the unadsorbed organic matter in the effluent was readily oxidizable and that failure to be oxidized earlier was the result of one or more of four factors:

1. The oxidizable materials were originally at too small a concentration for ready biological oxidation, and evaporation increased the concentration enough to support good growth of microorganisms.

2. Organic materials adsorbed by the carbon had been acting as inhibitors for biological oxidation; once they were removed, biological metabolism could proceed.

3. Time of contact in the sewage treatment plant was not great enough for complete oxidation of metabolites.

4. Short-circuiting in the sewage treatment plant allowed carryover of some readily oxidized substances.

In any event, there is preliminary evidence in this simple observation that a substantial fraction of the organic material leaking through the carbon column is not composed of so-called "persistent" compounds, but may instead be carbohydrates, amino acids, or low-molecular-weight carboxylic acid salts that would contribute little nuisance to receiving waters and would tend to be removed by biological oxidation processes in lakes or streams. Moreover, it means that further search for specific unadsorbed materials should not be confined to "exotic" chemicals but should include common metabolites and their intermediates.

Because of this experience, a portion of the sample number two was acidified with HCl prior to shipment from Cincinnati to suppress bacterial action.

General measurements made on the samples included organic carbon and COD of both total and filtered material, potentiometric acid-base titrations, and infra-red examinations of chloroform extractables. Individual measurements of ABS, carbohydrates, and dicarboxylic acids were attempted.

Total Organic Carbon

Organic carbon in the effluent samples was determined by the wet oxidation method described by Weber and Morris.[21] For each sample, total organic carbon determinations were performed on the unfiltered material so as to include insoluble organic matter, and on samples of the effluent that had been subjected to filtration. The samples were first acidified with sulfuric acid and then oxygen was bubbled through them for 10 minutes to remove CO_2.

Results of the determinations, the average of two or three tests in each instance, are shown in Table 12 for the samples as received in concentrated form and as computed for the original effluents.

Table 12. DETERMINATIONS OF ORGANIC CARBON IN EFFLUENTS FROM PITTSBURGH CARBON FILTERS

Sample	Organic carbon mg/liter in concentrate	Organic carbon mg/liter in effluent
No. 1, unfiltered	92	2.6
No. 1, filtered	66	1.8
No. 2, unfiltered	143	2.4
No. 2, filtered	50	0.83

Chemical Oxygen Demand

Determinations of COD were also carried out by the standard technique on unfiltered and filtered samples except that, because of the bacterial decomposition in sample No. 1 and other limitations on the sample, a measurement on filtered concentrate was not possible for this material. The results of these determinations are shown in Table 13.

Ordinarily one may expect the COD value for a waste to be about 2.5 to 3 times the organic carbon, the theoretical ratio for carbon in the zero oxidation state as in carbohydrate being 32/12 or 2.67. Furthermore, the total weight of organic matter will range around 2.5 times the organic carbon, 30/12 or 2.5 being the value for a simple carbohydrate.

Table 13. DETERMINATIONS OF COD ON EFFLUENTS FROM PITTSBURGH CARBON COLUMNS

Sample	COD mg/liter in concentrate	COD mg/liter in effluent
No. 1, unfiltered	398	11.0
No. 2, unfiltered	236	3.9
No. 2, filtered	113	1.9

Thus, for organic material with average oxidation number near zero, COD and total weight of organic matter will be approximately the same numerically.

The two factors tend, however, to change in opposite directions as the average oxidation number departs from zero. With butyric acid, $C_4H_{10}O_2$, with a mean oxidation number of -1.5 for the carbon, the weight is 1.875 times the organic carbon, while the COD should be 3.67 times the organic carbon. Similarly, for glyoxylic acid, $C_2H_4O_3$, with net carbon oxidation number of +1, the weight is 3.17 times the organic carbon, while the COD is only 2.0 times it.

Filtered sample No. 2 shows an expected ratio between COD and organic carbon, 113/50 or 2.26. If this ratio is accurate, the mean oxidation state of the carbon in the effluent is relatively high, about +0.6. Such a result seems in accord with the fact that this effluent had already been subjected to considerable oxidative treatment and is also in accord with the intuitive feeling that oxygenated organic compounds such as dicarboxylic acids, which will exist in wastes as ionized materials, will be less readily adsorbed by carbon than other types of organic substances will.

The ratios of COD to organic carbon for the unfiltered effluents, 4.33 for sample No. 1, and 1.65 for sample No. 2, are completely outside the range of legitimate values for the type of material being studied. Variations in sampling of the suspended matter or failure to achieve complete COD for suspended organic matter may have caused these anomalies.

Acid-Base Titrations

Because it seemed likely that carboxylic acid salts might be largely responsible for the observed leakage of organic material through carbon beds, it was felt that potentiometric acid-base titration curves on the effluent concentrates would be useful in characterizing the organic materials.

Accordingly, these titrations were performed on portions of the concentrates that had been filtered through membrane filters. Titrations were carried out on 25-milliliter portions of sample No. 1 and 50-milliliter portions of sample No. 2, pH readings with a glass electrode being taken frequently throughout the titrations with tenth-normal HCl or KOH. The results of these titrations, shown in Figures 75 and 76, were unsatisfactory largely because the dominating effect of the large concentrations of carbon dioxide, and bicarbonate alkalinity had been overlooked.

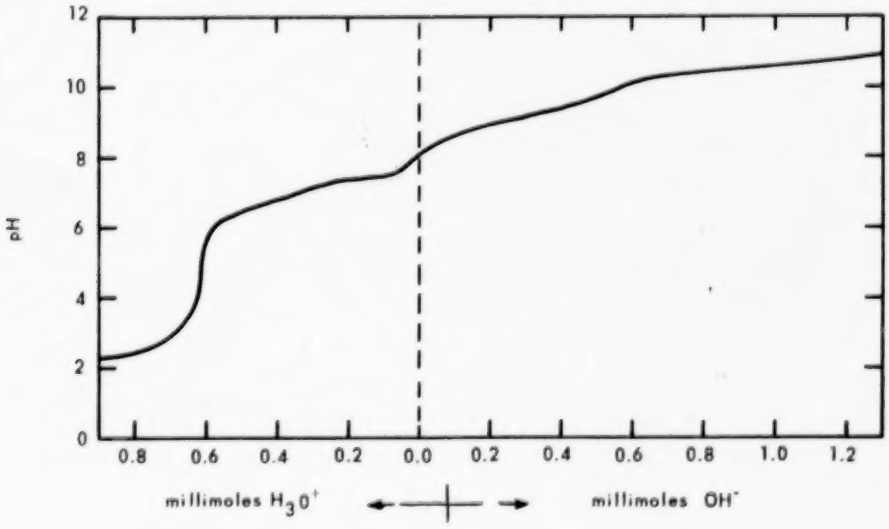

Figure 75. Titration of effluent No. 1, 25-ml sample.

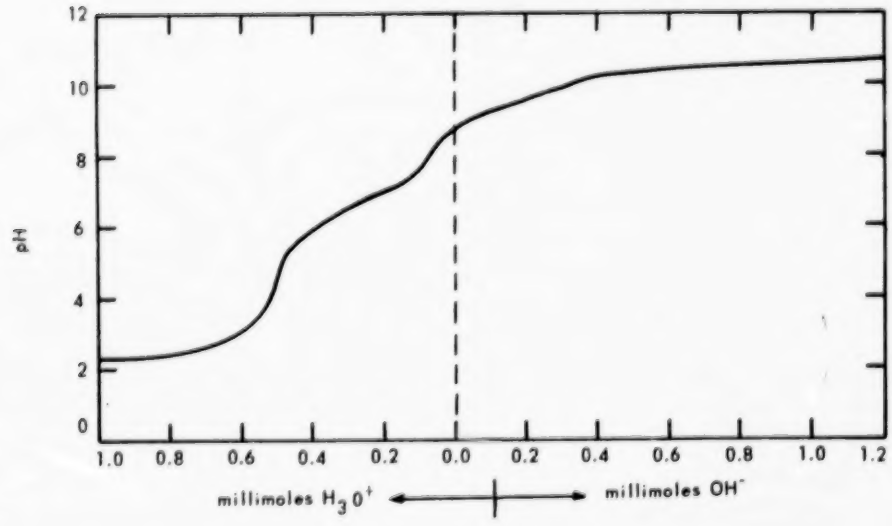

Figure 76. Titration of effluent No. 2, 50-ml sample.

Additional titrations were performed, therefore, on portions of filtered sample No. 2, which had been acidified and aerated to remove CO_2 before titration with tenth-normal hydroxide. Results of this work are shown in Figure 77.

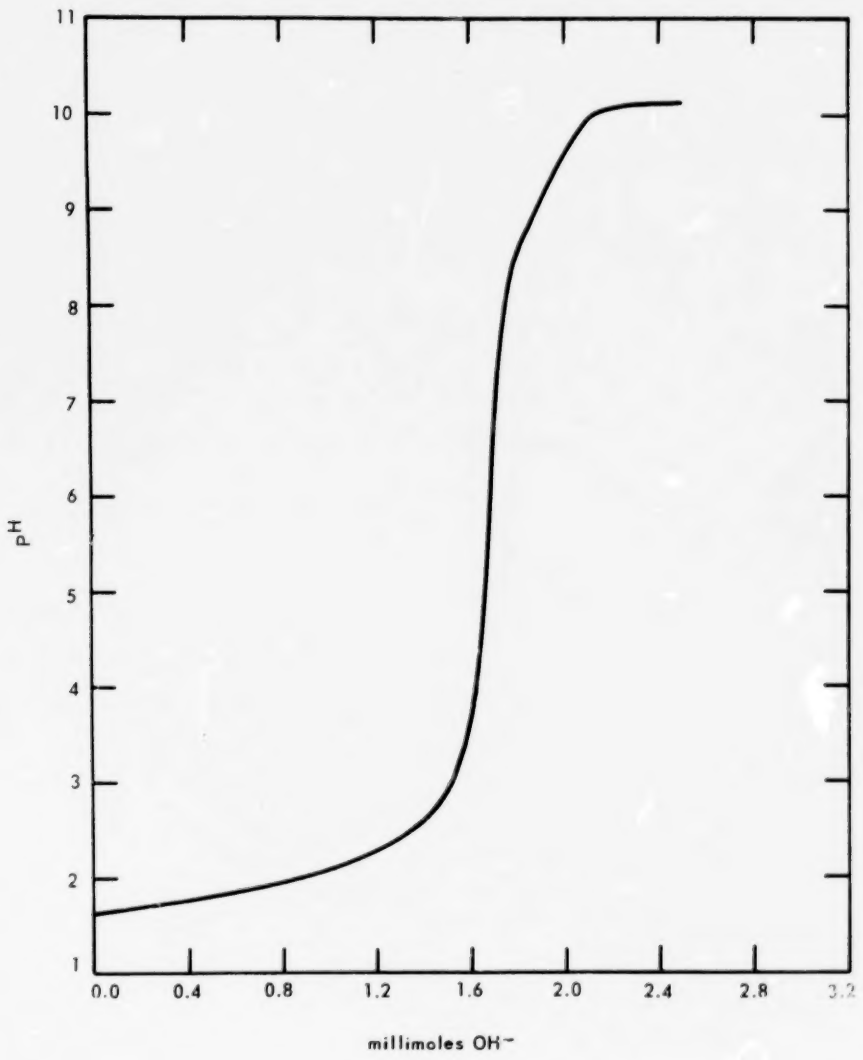

Figure 77. Titration of acidified effluent No. 1, 50 ml-sample.

Again the results were unsatisfactory, because the excess of acid used had been so great that neutralization of this strong acid tended to obscure the finer points of the titration curve. There was some indication of weakly basic constituents in the form of the titration curve near pH 10, possibly an indication of amino acids, but because precautions to remove ammonia and phosphate had not been taken, the data must be considered inconclusive.

In spite of the failure of these titrations, it is still believed that valuable information can be obtained from similar titrations carried out after more careful preparation of the initial solutions. Based on the experience obtained, preliminary treatment should include the following steps: (1) Acidification of total unfiltered sample to pH 4 + 0.5 followed by bubbling of nitrogen through the sample to remove CO_2 fully; neutralization with CO_2-free KOH, possibly accompanied by addition of Ca^{++} or some other precipitating ion to remove $PO_4^{\equiv}$ completely, followed by filtration (not necessarily through a membrane filter; it may be desirable to include colloidal material in the titration); (2) addition of CO_2-free KOH to pH 9.5 followed by bubbling of nitrogen to remove NH_3 fully. At this point the sample should be separated into two portions, one to be titrated carefully with dilute acid, the other with dilute base. As nearly continuous records of pH as a function of acid or base added should be obtained and compared with similar curves for the titration of CO_2-free distilled water.

ABS Determinations

Each of the concentrates was analyzed for ABS concentration by the methylene blue method as given in Standard Methods.[36]

Concentrations were determined from a calibration curve obtained for a technical ABS, Ultrawet DS, obtained from the Atlantic Refining Company, having a molecular weight of 372.[19] The Ultrawet DS solutions used for the calibration of the methylene-blue method were standardized by ultraviolet spectrophotometry.[19]

Sample No. 1 was determined to have an ABS concentration of 6.0 milligrams per liter, and sample No. 2 an ABS concentration of 7.0 milligrams per liter. Considerable difficulty was experienced with both effluents during the ABS tests owing to emulsion formation.

These values for ABS concentration in the concentrates correspond to 0.17 milligram per liter in the original effluent No. 1 and to 0.12 milligram per liter in effluent No. 2, values that accord well with expectations for effluents from carbon columns and with similar analyses performed at Cincinnati.

Miscellaneous Specific Tests

All the additional work carried out was on sample No. 2 because of the bacterial degradation that occurred rapidly in sample No. 1.

Attempts were made to find chloroform-extractable materials in the concentrate by treatment with this reagent followed by infra-red examination of the dried chloroform extracts. Only negative results

were obtained with the concentrates as received, and attempts to work with more highly evaporated solutions were frustrated by the formation of highly stable emulsions. Time did not permit further explorations along this line.

Glucose and total carbohydrate determinations were carried out, the former by the glucostat enzymatic method, the latter by the anthrone method as described by Gaudy.[37] Results for glucose were negative, as might well have been expected, but carbohydrate was found at a concentration of 7 milligrams per liter in the concentrate, corresponding to 0.12 milligram per liter in the initial effluent. One might guess that this material would be dextrin-like, degraded glycogen or cellulose perhaps.

Some experimentation was done with thin-layer chromatography on the effluent samples. Qualitative indication of the presence of small quantities of dicarboxylic acids was obtained, but methods for quantitative estimation of the amount were not at hand. The technique does show promise for examination of these effluents and probably should be pursued more intensively in the future.

Unfortunately, circumstances prevented extension of these investigations; additional general information could have been obtained readily. For example, determinations of Kjeldahl nitrogen and organic phosphorus would have helped greatly in characterizing the residues, and these can be performed easily. More sophisticated techniques such as gas chromatography were proposed, but could not be used because of delays in obtaining appropriate equipment.

Discussion

Perhaps the most significant result of this preliminary and partial investigation into the nature of the organic material unadsorbed by activated carbon columns is a negative one. No indications were found of important amounts of the persistent, noxious organic chemicals for which methods of removal are most important. What positive data could be obtained make it seem likely that partially oxidized substrates and metabolites of microorganisms make up a major portion of the effluent organic matter. Although this conclusion is not firm, nothing that has been found gives any reason to suppose that further development of full-scale equipment for advanced waste treatment by activated carbon should be drastically modified or abandoned.

Besides the obvious step of continued experimentation along the lines followed in these tests to find individual compounds or classes of compounds contributing to the organic leakage, another method of approach is to test likely individual substances or classes of materials to see how they behave on carbon columns. Dilute solutions of individual carbohydrates, carboxylic acids, amino acids, and so forth might

be passed through laboratory-scale columns to see how effectively they are removed.

Note that in the small-column studies described earlier the material that gave greatest difficulty with leakage was triethanolamine, a small, hydroxylated molecule existing largely in salt-like cationic form in neutral aqueous solutions. In contrast, all materials containing phenolic groups seem to be effectively adsorbed.

Apparently, if additional removal of organic matter beyond that now obtainable with reasonable depth of activated carbon is desired, one should follow the activated carbon with a contrasting type of adsorbent. One possibility seems to be to make use of porous or so-called "macroreticular" ion-exchange resins in this way, taking advantage of their adsorptive abilities rather than specifically of their ion exchange properties. Organic "fouling" of ion-exchange resins is well known and there is reason to suppose that the types of materials causing fouling may be like those leaking through carbon columns.

It is recommended that experimentation be initiated to investigate these possibilities.

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APPENDIX A

NOTATIONS

A = total external surface area of adsorbent, $[L]^2$

b = constant of Langmuir adsorption isotherm related to the energy of adsorption

a_m = effective transfer area per unit mass adsorbent, $[L]^2$

C = mass concentration of solute in effluent $[M]\ [M]^{-1}$

C_o = mass concentration of solute in influent $[M]\ [M]^{-1}$

C_s = mass concentration of solute in adsorbent $[M]\ [M]^{-1}$

ΔC = concentration potential across liquid film $[M]\ [M]^{-1}$

D = diameter of adsorbent particle, $[L]$

ξ = $k_T a_m M_a Q_m \pi / W\ (k_T a_m M_a + Q_m)$

h = height measured from base of expanded medium, $[L]$

h_e = total height of expanded medium, $[L]$

k & k_T = mass transfer coefficients, $[M]\ [L]^{-2}\ \ [T]^{-1}/\Delta c$

m & M_a = total mass of adsorbent, $[M]$

μ = dynamic viscosity of solution, $[M]\ [L]^{-1}\ \ [T]^{-1}$

N_R' = modified Reynolds number, dimensionless

π = partition factor = $\left(\frac{C}{C_s}\right)_{equil.}$, dimensionless

Q_m = mass flow rate, $[M]\ [T]^{-1}$

r = rate of transfer, $[M]\ [T]^{-1}$

ρ = mass density of solution, $[M]\ [L]^{-3}$

t = time, $[T]$

v = superficial face velocity, $[L]\ [T]^{-1}$

W = total weight of carbon, $[M]$

X = quantity of solute adsorbed per unit weight adsorbent, $[M]\ [M]^{-1}$

$X\infty$ = capacity of adsorbent at equilibrium with a solution of concentration C_o, $[M]\ [M]^{-1}$

X_m = moles of solute in forming a complete monolayer on the carbon surface, $[M]\ [M]^{-1}$

APPENDIX B

ADVANCED WASTE TREATMENT RESEARCH PUBLICATIONS

Although over-all guidance of AWTR research projects is provided by the AWTR Program, the results obtained, opinions expressed, and conclusions reached by the contractors are theirs and are not necessarily endorsed by the Federal Water Pollution Control Administration. Except for editorial review and abridgments as necessary, these reports appear as received from the contractors.

		Report Number
AWTR-1	Summary Report, June 1960 - December 1961	W62-9
AWTR-2	Preliminary Appraisal of Advanced Waste Treatment Processes	W62-24
AWTR-3	Ultimate Disposal of Advanced-Treatment Waste	999-WP-3
	Part 1. Wet Oxidation	
	Part 2. Incineration	
AWTR-4	Waste-Water Renovation	999-WP-4
	Part 1. A Design Study of Freezing and Gas Hydrate Formation	
	Part 2. Feasibility Tests of Freezing	
AWTR-5	Contaminant Removal from Sewage Plant Effluents by Foaming	999-WP-5
AWTR-6	Cost of Purifying Municipal Waste Waters by Distillation	999-WP-6
AWTR-7	Advanced Waste Treatment by Distillation	999-WP-9
AWTR-8	Ultimate Disposal of Advanced-Treatment Waste	999-WP-10
	Part 1. Injection	

		Report Number
	Part 2. Placement in Underground Cavities	
	Part 3. Spreading	
AWTR-9	Adsorption of Biochemically Resistant Materials from Solution. 1.	999-WP-11
AWTR-10	Feasibility of Granular, Activated - Carbon Adsorption for Waste-Water Renovation	999-WP-12
AWTR-11	Evaluation of the Use of Activated Carbon and Chemical Regenerants in Treatment of Waste Water	999-WP-13
AWTR-12	Evaluation of Varicus Adsorbents and Coagulants for Waste-Water Renovation	999-WP-14
AWTR-13	Electrochemical Treatment of Municipal Waste Water	999-WP-19
AWTR-14	Summary Report: The Advanced Waste Treatment Research Program. January 1962 through June 1964	999-WP-24
AWTR-15	Feasibility of Granular, Activated Carbon Adsorption for Waste-Water Renovation. 2.	999-WP-28
AWTR-16	Adsorption of Biochemically Resistant Materials from Solution. 2.	999-WP-33

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